# **DRAFT**

# METHIDATHION RISK CHARACTERIZATION DOCUMENT

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# ESTIMATION OF EXPOSURE OF PERSONS IN CALIFORNIA TO PESTICIDE PRODUCTS THAT CONTAIN METHIDATHION

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#### ABBREVIATIONS AND ACRONYMS

ADD Absorbed Daily Dosage

AADD Annual Average Daily Dosage

AI active ingredient

ARB California Air Resources Board CCR California Code of Regulations

CFAC California Food and Agriculture Code

CFR Code of Federal Regulations

CFWAP California Farm Worker Activity Profile

DFR dislodgeable foliar residue

DPR California Department of Pesticide Regulation

EAD Exposure Assessment Document

EC emulsifiable concentrate

FIFRA Federal Insecticide, Fungicide, and Rodenticide Act

IRED Interim Reregistration Eligibility Decision

LADD Lifetime Average Daily Dosage

LOD limit of detection

LOQ limit of quantification

M/L mixer/loader

M/L/A mixer/loader/applicator

NOAEL No-Observed-Adverse-Effect-Level

OP organophosphate

PHED Pesticide Handler Exposure Database
PISP Pesticide Illness Surveillance Program

PPE personal protective equipment

PUR Pesticide Use Report
REI restricted entry interval

SADD Seasonal Average Daily Dosage

TAC toxic air contaminant
TWA time-weighted average
UCL upper confidence limit

U.S. EPA U.S. Environmental Protection Agency

WP wettable powder

WSP water-soluble packaging

#### **ABSTRACT**

Methidathion (S-[(5-methoxy-2-oxo-1,3,4-thiadiazol-3(2H)-yl)methyl] O,O-dimethyl phosphoro-dithioate) is an organophosphate insecticide/miticide registered for control of agricultural pests. Both methidathion products registered in California are restricted use pesticides. Formulations include a wettable powder containing 25% active ingredient (AI) and an emulsifiable concentrate containing 24.4% AI. Methidathion is used on various crops, including citrus, stone and pome fruits, kiwifruit (24c label), nuts, artichokes, olives, safflower, sunflower, alfalfa (grown for seed only), cotton, and ornamental plants (nursery stock only). Almonds, citrus, artichokes, walnuts, and stone fruits are the predominant crops receiving methidathion applications in California.

Significant exposure scenarios were identified based on uses listed on product labels. A total of nine handler and three reentry scenarios were identified. As adequate exposure data were lacking, handler exposures were estimated using surrogate data from the Pesticide Handler Exposure Database, and reentry exposures were estimated using dislodgeable foliar residue data for methidathion and transfer factors from studies with surrogate chemicals. Exposure estimates were compared to estimates made by the U.S. Environmental Protection Agency.

Acute exposure estimates for pesticide handlers varied widely, with airblast applicators having the highest exposure estimates. Acute absorbed daily dosage (acute ADD) estimates for mixer/loaders (M/L) were 0.131, 0.158 and 1.15 mg/kg/day (handling products in support of airblast, groundboom and aerial applications, respectively); mixer/loader/applicator (M/L/A) acute ADD estimates were 0.0034 and 0.191 mg/kg/day (using low-pressure handwands and backpack sprayers, respectively); applicator acute ADD estimates were 0.177, 4.65 and 5.86 mg/kg/day (groundboom, aerial and airblast applications); and the acute ADD estimate for flaggers was 1.90 mg/kg/day.

Fieldworker exposure estimates were generally in the range of the lowest handler estimates. Estimated acute ADD was 0.093 mg/kg/day for cotton/safflower scouts, 0.007 mg/kg/day for workers harvesting/thinning citrus, and 0.014 mg/kg/day for workers thinning artichokes.

Ambient air exposures and bystander exposures during applications also were estimated. Acute ADD for methidathion was estimated to be 0.000110 mg/kg/day for infants and 0.000052 mg/kg/day for adults. Acute ADD for methidathion oxon was estimated to be 0.000047 mg/kg/day for infants and 0.000022 mg/kg/day for adults.

Bystander exposure estimates were based on air monitoring done 15 – 150 m from the edge of a Tulare County orange grove during an application. Acute ADD for bystander exposure to methidathion was 0.00177 mg/kg/day for infants and 0.00087 mg/kg/day for adults. Acute ADD for bystander exposure to methidathion oxon was 0.00052 mg/kg/day for infants and 0.00026 mg/kg/day for adults. These estimates were based on a 24-hour time-weighted average concentration and an assumption of typical activity levels. As available information suggests that exposures of less than 24 hours can result in toxicity, 1-hour absorbed dose estimates were calculated as well, based on the highest measured concentrations and an assumption of heavy

activity. These 1-hour absorbed dose estimates for methidathion were 0.00315 mg/kg/hr for infants and 0.00057 mg/kg/hr for adults. The 1-hour absorbed dose estimates for methidathion oxon were 0.00019 mg/kg/hr for infants and 0.000034 mg/kg/hr for adults. Seasonal and annual exposures for bystanders were not estimated, because airborne concentrations are anticipated to reach ambient levels within a few days after each application and limited numbers of applications are allowed by product labels.

#### INTRODUCTION

Methidathion (S-[(5-methoxy-2-oxo-1,3,4-thiadiazol-3(2H)-yl)methyl] O,O-dimethyl phosphoro-dithioate) is an organophosphate (OP) insecticide/miticide registered for control of agricultural pests. Like other OPs, it is a cholinesterase inhibitor. In California, methidathion is used on various crops, including citrus, stone and pome fruits, kiwifruit, nuts, artichokes, olives, safflower, sunflower, alfalfa (grown for seed only), cotton, and ornamental plants (nursery stock only).

Methidathion was first registered with the U.S. Environmental Protection Agency (U.S. EPA) in 1972, and in California in 1977. As of May 2006, two products were registered in California, both by Gowan Company. Methidathion is being evaluated in accordance with the California Food and Agriculture Code (CFAC) Section 12824 and the Birth Defect Prevention Act of 1984 (CFAC 13121-13135), based on possible adverse effects identified in chronic toxicity, oncogenicity and chromosomal aberrations studies. This Exposure Assessment Document (EAD) is the first prepared by the California Department of Pesticide Regulation (DPR) for methidathion, although DPR has conducted studies in which worker exposure was monitored (Maddy *et al.*, 1983; Wang *et al.*, 1987). A dietary and drinking water risk assessment has been done by DPR (Lewis, 2001), as required by the Food Safety Act of 1989 (Title 3 California Code of Regulations (3 CCR), Sections 13134-13135).

As part of its pesticide Reregistration Eligibility Decision process required by the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), U.S. EPA published a Health Evaluation Document for methidathion in 1999 (Travaglini, 1999), and released an Interim Reregistration Eligibility Decision (IRED) in March 2002 (U.S. EPA, 2002). In the IRED, U.S. EPA estimated occupational risk for several scenarios; exposure estimates used by U.S. EPA to calculate these risk estimates were given in Travaglini (1999), not in U.S. EPA (2002). Information and conclusions presented by Travaglini (1999) and U.S. EPA (2002) were considered by DPR during the preparation of this EAD. However, exposure scenarios considered by DPR differed somewhat from those considered by U.S. EPA. Additionally, several assumptions used in exposure assessments differed between DPR and U.S. EPA. Such differences are discussed in this EAD when appropriate.

The purpose of this EAD is to estimate exposures resulting from legal uses of methidathion in California. Exposure estimates from this EAD will be used by DPR in its risk assessment process to estimate risks of these exposures, and ultimately in the risk management process, to determine whether existing product labels, laws and regulations are sufficiently protective. To meet this purpose, the EAD reports on physical and chemical properties of methidathion that

might be pertinent to exposure, legal requirements governing use of methidathion products, studies monitoring concentrations of methidathion and its major degradate in the environment, and available information about likely exposures to methidathion. This information is incorporated into the exposure estimates that are reported in this EAD.

Occupational exposure to methidathion may be anticipated to occur during handling (mixing, loading, flagging, and application) and during reentry activities, such as scouting, thinning and harvesting of crops that have received foliar applications of methidathion. Pesticide handlers include mixer/loaders (M/L), mixer/loader/applicators (M/L/A), applicators, and flaggers. Reentry activities include any cultivation, harvest or other activity occurring post-application. Additionally, methidathion was detected in monitoring of ambient air in some urban and rural areas and in air near application sites, suggesting that public exposure to airborne methidathion might occur.

#### FACTORS DEFINING EXPOSURE SCENARIOS

#### **Physical and Chemical Properties**

Methidathion has moderate water solubility and a low vapor pressure. Technical methidathion is fairly stable in storage, with 2% decomposition in 12 months at 20 - 25°C, and 10% decomposition in 12 months at 35°C (Lail, 1991). Physical and chemical properties for methidathion are listed below (Daly, 1987; Wiler, 1987; Rordorf, 1988; Verma, 1988; Lail, 1991; Tomlin, 1994).

CAS Registry No.: 950-37-8

• Structural Formula: 
$$H_3C$$
 $N-N$ 
 $S$ 
 $O$ 
 $CH_3$ 
 $CH_2$ 

• Empirical Formula: C<sub>6</sub>H<sub>11</sub>N<sub>2</sub>O<sub>4</sub>PS<sub>3</sub>

• Molecular weight: 302.3 g

• Solubility: Water (22°C and pH 4): 221 mg/L

• Solvents (all at 20°C):

Cyclohexane: 850 g/L

Acetone: 690 g/LXylene: 600 g/L

Ethanol: 260 g/L

• n-Octanol: 53 g/L

• Vapor pressure:  $3.37 \times 10^{-6}$  mmHg at 25°C

• Octanol/water partition coefficient: 166 ( $\log K_{ow} = 2.2$ )

• Henry's law constant:  $1.95 \times 10^{-9}$  atm•m<sup>3</sup>/mole at 22°C

#### Formulations and Uses

Two methidathion products were registered in California as of May 2006, both by Gowan Company. These products include one 25% active ingredient (AI) wettable powder (WP) and one 24.4% AI emulsifiable concentrate (EC) product. The WP product is packaged in water-soluble packaging (WSP). The EC product has multiple packaging types, which include WSP. For EC products, each pint of liquid is equivalent to ½ lb AI; thus, one gallon equals 2 lbs AI. All products are classified by U.S. EPA as restricted-use pesticides due to concern about residue effects on avian species (Title 40 Code of Federal Regulations (40 CFR), Section 152.170), and are listed as restricted-use pesticides under California regulations as well (3 CCR 6400).

Registered uses are as an insecticide and miticide on various crops, including citrus, stone, and pome fruits, nuts, artichokes, olives, safflower, sunflower, cotton, and ornamental plants (nursery stock only). Special Local Needs uses (FIFRA Section 24c) have also been approved for pest problems within all or part of California. These are summarized in Table 1. The pests, application rates, and other conditions summarized in Table 1 are relevant only to applications made under the Special Local Needs labels.

Table 1. Special Local Needs (24c) Registrations for Methidathion in California <sup>a</sup>

Number	Crop	Pest	Application Rate (lb AI/acre) <sup>b</sup>	Pre-harvest Interval (Days) <sup>c</sup>
CA-010009	Citrus	California Red Scale	$3.0 - 4.0^{d}$	60
CA-010011	Clover grown for seed	Certain Insects <sup>e</sup>	1.0	Not applicable
CA-010002	Alfalfa grown for seed	Lygus, Leafhoppers, Weevil	1.0	Not applicable
CA-020002	Timothy or Timothy- alfalfa grass <sup>f</sup>	Grass Scale, Thrips, Spider Mites	0.5 - 1.0	21
CA-040023	Kiwifruit <sup>g</sup>	Scale Insects	$1.5 - 2.0^{d}$	15

<sup>&</sup>lt;sup>a</sup> As of May 2006. Registrations for Supracide 25W (CA-010009 and CA-010011) and Supracide 2E (CA-010002, CA-020002, and CA-040023). Restrictions noted in this table apply to these registrations only.

Table 2 summarizes methidathion use in California for the five year period, 2000-2004 (DPR, 2001; 2002; 2003; 2005; 2006a). In addition to providing total applications to all crops, Table 2 lists applications to several crops where usage was greatest, as well as some limited-use crops such as cotton that are specifically addressed in the Exposure Assessment section. Crops are listed in Table 2 in descending order, based on pounds AI applied in 2004.

<sup>&</sup>lt;sup>b</sup> Pounds active ingredient (AI) per acre. Multiply value by 1.12 to get application rate in kg AI/ha.

<sup>&</sup>lt;sup>c</sup> Restricted entry interval (REI) is 48 hours for all of these, except CA-010009, which is 40 days.

<sup>&</sup>lt;sup>d</sup> Application by ground rig only.

<sup>&</sup>lt;sup>e</sup> Includes Lygus, leafhoppers, aphids, weevil and Lepidoptera pests. A maximum of two applications/season is allowed. <sup>f</sup> Use is only allowed in Lassen, Modoc, Shasta, and Siskiyou counties.

g Dormant application only. One spray allowed per year.

Table 2. Methidathion Use in California from 2000 through 2004 <sup>a</sup>

Crop	2000		2001		2002		2003		2004	
	Lbs AI	<u>%</u>	<u>Lbs AI</u>	<u>%</u>	Lbs AI	<u>%</u>	Lbs AI	<u>%</u>	Lbs AI	<u>%</u>
Artichokes	15,331	15.6	14,285	15.4	11,920	17.6	4,871	9.0	12,010	19.6
Citrus <sup>b</sup>	6,972	7.1	20,147	21.7	16,040	23.6	14,369	26.4	11,752	19.2
Almonds	25,120	25.6	23,105	24.8	10,974	16.2	10,216	18.8	10,126	16.5
Peaches	13,504	13.8	7,386	7.9	5,605	8.3	5,823	10.7	4,314	7.0
Plums	10,568	10.8	7,981	8.6	1,636	2.4	4,136	7.6	3,751	6.1
Olives	611	0.6	627	0.7	3,023	4.5	2,505	4.6	3,178	5.2
Alfalfa	570	0.6	1,555	1.7	287	0.4	762	1.4	3,059	5.0
Walnuts	5,130	5.2	3,115	3.3	2,879	4.2	5,138	9.4	2,751	4.5
Nursery	368	0.4	408	0.4	376	0.6	342	0.6	2,635	4.3
Prunes	7,454	7.6	3,668	3.9	2,073	3.1	912	1.7	867	1.4
Safflower	212	0.2	664	0.7	613	0.9	1,235	2.3	698	1.1
Cotton	32	0.0	61	0.0	0	0.0	103	0.2	0	0.0
Misc. crops <sup>c</sup>	12,257	12.5	10,053	10.8	12,457	18.4	3,986	7.3	6,063	9.9
All crops	98,129	100	93,055	100	67,833	100	54,398	100	61,204	100

<sup>&</sup>lt;sup>a</sup> Expressed as lbs active ingredient (AI), and as percent of total methidathion use for each year (DPR, 2001; 2002; 2003; 2005; 2006a).

Use of methidathion decreased somewhat during the five-year period (Table 2). Several reasons have been reported for decreasing reliance on methidathion. For example, methidathion is one of the broad-spectrum insecticides in which resistance has developed in the California red scale, a major citrus pest in the San Joaquin Valley (Citrus Research Board, 2003). Also in oranges (the citrus crop receiving most methidathion applications) mineral oil has been increasingly used as a low-cost insecticide; uses of newer, lower risk insecticides such as imidacloprid and acetamiprid have increased substantially as well (DPR, 2005). In almonds, many growers have switched from OPs to pyrethroids for dormant season applications, due to concerns about surface water contamination with OPs (Epstein and Bassein, 2003; Zhang *et al.*, 2004).

In spite of the trend of decreasing methidathion use in recent years, there is no mechanism in place to prevent increased use in the future. Because of this, decreased use documented in a single year (e.g., 2004) was not considered to be necessarily representative of future methidathion use for purposes of estimating exposure. Exposure estimates in this EAD rely on five-year average use patterns rather than data from any single year. The most recent five years shown in Table 2 include three years (2002 – 2004) during which use was substantially lower than in previous years. The highest reported annual use of methidathion (since 1990, when pesticide use reporting began in California) was 451,826 lbs in 1993 (DPR, 2001). This is more than four times the use in 2000, and is more than eight times the use reported in 2003.

<sup>&</sup>lt;sup>b</sup> Oranges were the dominant citrus crop, accounting for 64% - 92% of all methidathion applied to citrus each year.

<sup>&</sup>lt;sup>c</sup> Includes crops such as kiwifruit, apples, nectarines, pears, apricots, cherries, etc.

In 2000 – 2004, methidathion use was most prevalent along the central coast (e.g., Monterey County) and in the San Joaquin and Sacramento valleys. This use pattern can be seen in Table 3, which lists for each of five high-use crops, the three counties having the greatest methidathion use (lbs AI applied) in 2004. Nut crops (e.g., almonds) are mostly grown in the southern San Joaquin and the northern Sacramento valleys. Deciduous fruits (e.g., peaches) grow throughout the San Joaquin and Sacramento valleys. Citrus crops are grown primarily in the warmer, drier, southern San Joaquin valley. In contrast, artichokes are grown in the cool, well-drained soils of the central and southern coasts. In Table 3, the number of applications reported statewide for each crop is also given. Fewer applications have been reported in recent years as methidathion use has decreased

Table 3. Counties with Greatest Reported Methidathion Use on Selected Crops in 2004 a

Use Site	No. Apps. <sup>b</sup>	County (	Total in listed counties (%) <sup>d</sup>		
Artichokes	325	Monterey (98.1)	Santa Barbara (1.2)	Santa Clara (0.4)	99.7
Citrus	151	Kern (46.7)	Tulare (31.8)	Fresno (17.5)	96.0
Almonds	141	Kern (40.5)	Stanislaus (22.9)	San Joaquin (20.0)	83.3
Peaches	151	Sutter (20.5)	Stanislaus (19.9)	Kern (16.7)	56.3
Plums	71	Kern (81.4)	Tulare (14.1)	Sutter (1.6)	97.1

<sup>&</sup>lt;sup>a</sup> Three leading counties based on total reported use (lbs active ingredient in each county) in 2004 (DPR 2006b; guery run May 12, 2006).

Methidathion is applied using aircraft, ground boom sprayer, airblast sprayer, low-pressure handwand, and backpack sprayer. Chemigation (application through an irrigation system) is prohibited. Products may also be applied directly to the soil by injection, shank or chisel. The WP and EC products are registered for nearly identical uses, except that the EC product may be used on sunflowers and nursery stock in California, whereas the WP product is not registered for those uses.

Application rates range from 0.25 to 5 lbs AI/acre. The application rate for most tree crops is 4 to 12 lbs of product (1 to 3 lbs AI) per acre per application, except for citrus fruit, which may receive up to 20 lbs of product per acre (5 lbs AI/acre). Application rates for row and field crops are lower, 2 to 4 lbs of product (0.5 to 1 lb AI) per acre. For deciduous fruit and nut trees, the product is diluted in a minimum of 20 and 50 gallons of water per acre for aerial and ground application, respectively. For citrus and olives, the product is diluted in a minimum of 20 and 400 gallons of water per acre for air and ground, respectively.

Generally, only one dormant application per season is made for the deciduous fruit and nut crops, and nursery stock including woody ornamentals and herbaceous plants. Artichokes may receive up to eight applications per year and safflower up to three. Citrus may receive

<sup>&</sup>lt;sup>b</sup> Number of applications to the crop in California reported in 2004. Total number of methidathion applications to all crops in 2004 was 1,222. The applications to crops shown in this table total 829, or 69% of all applications in California.

<sup>&</sup>lt;sup>c</sup> Percent of total pounds applied to the crop in California applied in the three listed counties.

<sup>&</sup>lt;sup>d</sup> Sum of percent use in top three counties (e.g., all but 0.3% of use in artichokes occurred in the listed counties).

applications anytime except during the bloom period or two weeks before harvest, with a maximum of two applications per growing season. Pre-harvest intervals range from 7 days for walnuts and 14 days for cotton, to 80 days for almonds. In artichokes and olives, applications are prohibited after bud formation.

#### **Label Precautions**

As with other pesticide products, methidathion product labels contain information pertinent to exposure estimates for both handlers and reentry workers. The Worker Protection Standard requires handlers to wear protective clothing and equipment specified on the label (40 CFR 170.240). As the purpose of this EAD is to estimate exposures resulting from legal uses, handlers are assumed to wear clothing and protective equipment specified on the product label unless exempted by regulation as discussed below. No additional protective clothing or equipment, beyond that which is legally required, is considered in exposure estimates. The WP and EC formulations of methidathion differ in acute toxicity, and require slightly different personal protective equipment (PPE) and engineering controls. Supracide® 2E is category I pesticide and requires the signal word "danger" on the label. Supracide® 25 W is a category II pesticide, carrying the signal word "warning."

The following clothing is required to be worn by handlers mixing, loading or applying products containing methidathion: long-sleeved shirt and long pants, chemical resistant (for EC) or waterproof (for WP) gloves, shoes plus socks. Protective eyewear is required when handling EC products. Use in enclosed areas requires a respirator with either an organic vapor-removing cartridge and a prefilter approved for pesticides (prefix TC-23C), or a canister approved for pesticides (prefix TC-14G). Respiratory protection is not required when handling WP, as it is in WSP. When EC products are handled outdoors, use of a dust/mist-filtering respirator is required (but see below in the California Requirements section).

Reentry workers do not have clothing and PPE requirements. Instead, the Worker Protection Standard prohibits workers from entering treated agricultural crops for the restricted entry interval (REI) specified on the product label (40 CFR 170.112). The REI stated on methidathion product labels is 48 hours when methidathion is applied at  $\leq$  2 lbs AI/acre and 14 days when applied at  $\geq$  2 lbs AI/acre (but see below under "California Requirements"). Additional PPE is required for early entry. Early entry that involves contact with treated surfaces requires that workers wear coveralls, for both products.

#### California Requirements

#### **Closed System for Mixing/Loading**

California regulations require the use of a closed system for handlers mixing and loading liquid formulations of toxicity category I pesticides (3 CCR 6746). Thus, any EC product not in WSP requires the use of a closed system for mixing and loading. Additionally, under California regulations, "Persons properly mixing pesticides packaged in water soluble packets are considered to be using a closed (mixing) system" (3 CCR 6738). All WP products are packaged

in water-soluble bags, as are some EC products (Rosenheck, 1998c). Because of the legal requirement (for EC products) and the legal definition of water-soluble packaging as a closed system, in this EAD handlers were assumed to mix/load using a closed system.

#### **Protective Clothing and Personal Protective Equipment**

Handlers mixing/loading using a closed system are allowed by federal and state regulations to substitute alternate, usually less protective PPE for that listed on product labels. Under the federal Worker Protection Standard (40 CFR 170.240), "Persons using a closed system to mix or load pesticides with a signal word of DANGER or WARNING may substitute a long-sleeved shirt, long pants, shoes, socks, chemical-resistant apron, and any protective gloves specified on the labeling for handlers for the labeling-specified personal protective equipment." Additionally, under the Worker Protection Standard, "Persons using a closed system that operates under pressure shall wear protective eyewear."

The corresponding California regulations have more restrictive PPE requirements (3 CCR 6738): "Persons using a closed system to handle pesticide products with the signal word 'DANGER' or 'WARNING' may substitute coveralls, chemical resistant gloves, and a chemical resistant apron for personal protective equipment required by pesticide product labeling." Also, "Persons using a closed system that operates under positive pressure shall wear protective eyewear in addition to the personal protective equipment listed..."

As stated in the previous section, methidathion product labels specify that handlers must wear long-sleeved shirt and long pants, chemical resistant (for EC) or waterproof (for WP) gloves, shoes plus socks. Depending on the product and conditions of use, appropriate respiratory protection is required, and protective eyewear is required when handling EC products. However, neither coveralls nor a chemical apron is required. Coveralls and chemical resistant aprons provide substantial protection (Thongsinthusak *et al.*, 1991); because of this, exposure estimates would be decreased if handlers were assumed to wear coveralls and chemical resistant aprons. Both the federal Worker Protection Standard (40 CFR 170.240) and the corresponding California regulation (3 CCR 6738) state that PPE *may* be substituted; that is, substitution of PPE during use of a closed system is optional. Handlers may legally wear protective clothing and PPE listed on products labels, and in this EAD all handlers were assumed to wear protective clothing and to use PPE listed on product labels. The exception to this was aerial applicators, who are not required to wear gloves during an application (3 CCR 6738). Exposure estimates were adjusted for the protective clothing and PPE as explained in the Exposure Assessment section.

#### **Restricted Entry Interval**

Methidathion applied to citrus has a longer REI, 30 days, under California regulation (3 CCR 6772); this extended REI has been required since 1976 and was incorporated into the exposure estimate for fieldworkers harvesting/thinning citrus. Exposure estimates for other crops used REIs specified on product labels.

#### **Reported Illnesses**

Reports of illness and injury with definite, probable, or possible exposure to pesticide products are recorded in a database maintained by the Pesticide Illness Surveillance Program (PISP) at DPR. The PISP database contains information about the nature of the pesticide exposure and the subsequent illness or injury. Between 1992 and 2003, a total of 39 incidents involving methidathion were reported to PISP (Mehler, 2005). In 2004 no illnesses related to methidathion exposure were reported to DPR (Louise Mehler, personal communication, May 11, 2006). Of the reported incidents, ten were associated with exposure (or possible exposure) to methidathion only, and the remaining 29 followed exposure (or possible exposure) to methidathion in combination with other pesticides. Most of the illnesses were systemic in nature (28 of 39, or 72% of the total cases), with complaints of nausea, vomiting, abdominal cramps, headache, and dizziness (Mehler, 2005). The other 11 cases consisted of injuries to, or irritation of eyes, skin or respiratory tract (several of the cases with systemic illnesses also had injuries to or irritation of the eyes, skin or respiratory tract). All but one of the cases involved occupational exposures, in which the subjects were working with or near methidathion (or multiple pesticides that included methidathion), or were working in treated areas. The exception was a drift incident of a person doing yard work.

Of the 38 individuals reporting illness following occupational exposures, seven were mixer/loaders and 19 were applicators. Five workers reported illness after entering a field treated with methidathion. Most of the other occupational exposures occurred when workers experienced drift from an application occurring nearby.

No deaths were associated with methidathion exposure. In an investigation of case reports of individuals with pesticide-associated illness between 1982 and 1990, methidathion was among ten organophosphates for which exposure was associated with cholinesterase inhibition in at least ten cases (O'Malley *et al.*, 1994).

Illness reports in the literature are limited to cases of ingestion (Teitelman *et al.*, 1975; Zoppellari *et al.*, 1990; Tsatsatkis *et al.*, 1996). Symptoms were generally consistent with organophosphate toxicity, and included substantial inhibition of cholinesterase activity when tested.

#### **Significant Exposure Scenarios**

U.S. EPA identified twelve major handler exposure scenarios for methidathion (Travaglini, 1999; U.S. EPA, 2002). Four of the scenarios involved aerial application: mixing/loading water-soluble packets, mixing/loading liquid formulations, fixed-wing aerial application, and flagging. Eight scenarios involved ground applications: mixing/loading water-soluble packets for groundboom applications, mixing/loading water-soluble packets for airblast applications, mixing/loading liquid formulations for groundboom applications, mixing/loading liquid formulations for airblast applications, groundboom sprayer application, airblast spray application, mixer/loader/applicator applying with a low-pressure handwand, and mixer/loader/applicator applying with a backpack sprayer.

In addition to the pesticide handler scenarios, U.S. EPA identified three groups of scenarios associated with post-application exposure (Travaglini, 1999; U.S. EPA, 2002). The first of these was scouting in cotton and safflower. The second was hoeing, irrigation, and other activities associated with artichokes. The third included harvesting and cultivation activities in tree crops such as citrus, kiwifruit, longan, and carambola.

Based on use instructions on current product labels, DPR identified scenarios that could result in significant occupational exposure. For handlers, DPR identified nine potentially significant exposure scenarios. Three of the scenarios involved aerial application: mixing/loading, application, and flagging. Six scenarios involved ground applications: mixing/loading in support of groundboom applications, mixing/loading in support of airblast applications, groundboom sprayer application, airblast spray application, mixing/loading/applying with a low-pressure handwand, and mixing/loading/applying with a backpack sprayer.

Other in addition to handlers, including reentry workers, bystanders, and the public, also have the potential for exposure to methidathion. Based on information about cultivation activities in crops for which methidathion is registered, DPR identified three potentially significant reentry worker exposure scenarios. These included scouting in cotton and safflower, harvesting and thinning citrus, and thinning artichokes. Estimates generated for scouting in cotton/safflower were anticipated to also be the best estimates available for exposures during other fieldworker activities in these crops, such as weeding, roguing, and harvesting. Exposures of reentry workers in other field crops such as alfalfa and timothy grass would be expected to be lower than those of cotton/safflower scouts, suggesting that protecting cotton/safflower scouts would protect workers in these other crops as well.

Harvesting and thinning activities in reentry worker exposure scenarios prepared by DPR were limited to citrus trees, rather than all tree crops, as deciduous fruit and nut trees receive only dormant applications. Kiwifruit vines also receive only dormant applications (Table 1). As no applications are allowed during the growing season, worker exposure to pesticides applied to fruit and nut trees and kiwifruit vines is expected to be minimal. Harvesting of artichokes also would not be expected to result in significant exposure to methidathion, as use occurs only in the interval between planting/cut-back and bud formation, suggesting that no significant residues would be anticipated at harvest.

Individuals might be exposed to methidathion if they live, work, or perform other activities adjacent to fields that are being treated or have recently been treated (bystander exposure). Also, air monitoring studies in Tulare County suggest that airborne methidathion exposures to the public are possible in areas that are far from application sites (ambient air exposure). Ambient air and bystander exposures to airborne methidathion were estimated, based on monitoring studies of methidathion and its reaction product, methidathion oxon, at an application site and in ambient air. Residential handler and reentry exposures are not anticipated to be significant, as methidathion has no registered uses in residential settings; all registered uses are agricultural. U.S. EPA concluded that residential exposure is limited to dietary and water (U.S. EPA, 2002). Exposures from water and diet are expected to be non-significant, based on evaluations by U.S. EPA (2002) and DPR (Lewis, 2001).

#### **PHARMACOKINETICS**

#### **Dermal and Inhalation Absorption**

No human dermal absorption studies were available during the preparation of this EAD, nor did U.S. EPA have access to dermal absorption studies while preparing the human health risk assessment for methidathion (U.S. EPA, 2002). DPR is aware of a single dermal absorption study, which used mice (Simoneaux and Marco, 1984). However, this study is considered unacceptable because organic solvents were used as vehicles (acetone and "petroleum hydrocarbon"), and because the study incorporated just a single dose. Organic solvents can influence absorption (U.S. EPA, 1998a), and use of a single dose provides insufficient information as dermal absorption may be dose-dependent (Thongsinthusak et al., 1999). U.S. EPA (2002) estimated the dermal absorption to be 30%, based on a comparison of oral and dermal toxicity in two studies using rabbits. Approximation of the dermal absorption by the ratio of oral to dermal toxicity studies is problematic because: 1) it depends on the assumption that all of the difference between oral and dermal lethal toxicity is due to dermal absorption, which may not be valid for most pesticides, 2) it depends on the assumption that 100% of an oral dose is absorbed, 3) toxicity studies use much higher doses than are typically of interest for dermal absorption and the ratio may not generalize to lower doses, and 4) dose determination in toxicity studies may not be sufficiently exact for determining dermal absorption. It is DPR policy not to use toxicity ratios to estimate dermal absorption.

As no acceptable data are available, the DPR default value of 50% was used in this document for calculations of absorbed dermal doses (Donahue, 1996). This default value is based on a review of data from forty pesticides, twenty-six of which were documented in Thongsinthusak *et al.* (1993).

No inhalation absorption studies are available. In the absence of these data, a default inhalation absorption value of 100% was used for calculations of doses absorbed via inhalation.

#### **Animal Metabolism**

Metabolism of methidathion has been investigated in mammals, including mice, rats, and cattle. Szolics (1987) investigated the fate of  $^{14}$ C-methidathion in rats after a single oral dose and after feeding methidathion in the diet for two weeks. Although the two-week dietary study will not be discussed in this exposure assessment, it might be important in estimating tissue residues after a subacute ingestion of methidathion. In the single-dose oral study,  $^{14}$ C-methidathion in a starch suspension was administered by oral gavage to two groups of ten rats (five male and five female); one group received 0.314 mg/kg and the other group 2.985 mg/kg (Szolics, 1987). Combined oral, fecal and urinary  $^{14}$ C recovery was 98-102%. The major routes of excretion were urine and exhaled air; elimination by these routes was approximately equal (study means were 39.7% of dose recovered from urine and 39.3% recovered from exhaled air). Mean half-lives for  $^{14}$ C were  $9.2 \pm 0.3$  hours and  $7.4 \pm 0.3$  hours for low-dose males and females, respectively, and  $7.5 \pm 0.6$  hours and  $8.9 \pm 0.7$  hours for high-dose males and females. Kinetics

of metabolism and elimination were similar for males and females, and consistent with a one-compartment model (Szolics, 1987).

Several urinary metabolites were identified in four male rats receiving a single oral dose of <sup>14</sup>C-methidathion, including the sulfide, sulfoxide, sulfone, and desmethyl derivatives (Cassidy *et al.*, 1969). The sulfoxide metabolite was the dominant one, accounting for 52% of the radioactivity excreted in the first 24 hours after dosing.

Min et al. (2005) determined urinary dialkyl phosphate metabolites in the urine of rats dosed both orally and dermally with methidathion. Oral or dermal doses were administered to two groups of five adult male Sprague-Dawley rats, with propylene glycol as the vehicle. The oral dose was 2.16 mg in 5 ml solution per kg body weight; as rats ranged in weight from 0.18 to 0.20 kg, the dose was administered in approximately 1 ml solution. The dermal dose, 66.5 mg dissolved in 5 ml solution per kg body weight, was applied to a clipped 6.25 cm<sup>2</sup> area on the back and sides of each rat. The dermal dose was kept in place for 96 hours, covered by a "semiocclusive dressing." For both oral and dermal routes, most of the dose was not accounted for by the measured dialkyl phosphate metabolites; total recovery of the oral dose averaged 15.4 + 3.4%, and the dermal dose recovery averaged 2.8 + 0.9%. The relatively low amount recovered from the dermal dose compared to oral is perhaps not surprising, as 66.5 mg applied to 6.25 cm<sup>2</sup> would be equivalent to a dermal dose of 10.6 mg/cm<sup>2</sup>. This is extremely high for a dermal dose. U.S. EPA (1998a) stated that the "maximum practical dose" for dermal absorption is 1 mg/cm<sup>2</sup> and recommended that dermal doses not exceed 0.01 mg/cm<sup>2</sup> to avoid saturation of absorption processes. The relatively high dose might be anticipated to result in a lower relative absorption. Following the oral dose, dialkyl phosphate metabolites were detected in urine for up to 48 hours; metabolites were detected up to 168 hours following the dermal dose (Min et al., 2005).

The metabolism of methidathion was studied *in vitro* using subcellular liver fractions from rats and mice, with and without the addition of cofactors glutathione and NADPH (Chopade and Dauterman, 1981). Metabolism was similar between the two species' livers, with a major metabolite being desmethyl methidathion. Desmethyl methidathion was one of four water-soluble metabolites; the other three were cysteine, glutathione, and cysteinyl glycine conjugates of methidathion.

In addition to studies in rodents, a few investigations were done on metabolism in cattle. In one study, methidathion radiolabeled at the carbonyl carbon was administered to three four-year-old Holstein cows (Polan and Chandler, 1971). Doses were given in capsules daily for 16-31 days. As with rats, metabolism and excretion was rapid, and approximately equal amounts of radiolabel were excreted in the urine and exhaled air. Metabolites appeared in milk and totaled less than 2% of the administered radiolabel; most of these metabolites were non-extractable and were not identified, although a small proportion were identified as sulfoxide and sulfone metabolites. Methidathion was not detected in milk (Polan and Chandler, 1971).

#### ENVIRONMENTAL CONCENTRATIONS

#### Air

California has laws that limit ambient air concentrations of pesticides, including the Toxic Air Contaminants Act (California Health and Safety Code, Sections 39650-39761), which codified the state program to evaluate and control toxic air contaminants (TAC). A pesticide is placed on the TAC list if its concentrations in ambient air have been determined to be within an order of magnitude of the concentration determined to cause human health effects (3 CCR 6890). Methidathion is a candidate for inclusion on the TAC list (Kollman, 1995). Methidathion concentrations have been monitored in the ambient air during peak application season and in the air adjacent to an application site. These studies are discussed below. Additionally, a study done by DPR in January 1989 measured methidathion concentrations in fog water collected with an active sampler consisting of Teflon tubing and a pump, as well as in vegetation and on cards placed among crops (Turner et al., 1989). Although Turner et al. (1989) did not monitor methidathion concentrations in air, the results of the study suggest that methidathion can be transported atmospherically for distances of at least 0.4 km. This study was done in Stanislaus County, in response to observations that residues of certain pesticides, including methidathion, were found on crops where they had not been used; these crops were adjacent to orchards where dormant spray pesticides, including methidathion, were used in winter. Methidathion concentrations were above the minimum detection limit in nearly all fog water samples, with estimated fog water in air concentrations (based on volume of fog in air sampled by the collection pump) ranging from 0.00008 to 0.00097 µg/m<sup>3</sup>. Methidathion was also detectable in vegetation and card samples. As methidathion was not applied within 0.4 km of the sample sites, these results suggest that atmospheric transport occurred.

#### **Ambient Air**

In 1991, ambient air monitoring of methidathion and methidathion oxon was conducted in Tulare County under contract to the Air Resources Board (ARB) of the California Environmental Protection Agency (Royce *et al.*, 1993a). Tulare County was chosen for ambient air monitoring because it was the county with the most methidathion use. Samples were collected during a four-week interval, from June 27 through July 25, at four sites near anticipated methidathion applications, and at one background site.

The four ambient sites were all within 0.25 miles (0.16 km) of citrus groves, a major use site for methidathion, in the following locations: one at the Sunnyside Union Elementary School, Strathmore (Site S); one at Jefferson Elementary School, Lindsay (Site J); one at Exeter Union High School, Exeter (Site E); and one at the University of California Lindcove Field Station, Exeter (Site UC). The background site was the ARB Ambient Air Monitoring Station, Visalia (Site B). Except for Site UC, where the sampler was located 1.8 m above ground in an open area, all samplers were taken from rooftops 2-15 m above ground. Sample devices consisted of a glass tube containing two sections of XAD-2 resin (a 400-mg primary and 200-mg backup section) connected to a flowmeter and sampling pump with Teflon tubing; two resin tubes and flowmeters were connected to a very low flow sampling pump with nominal flow rate of 4 L/min (Royce *et al.*, 1993a).

Quality assurance consisted of replicate sampling, control spikes with each set of samples extracted, and laboratory and field blanks (Royce *et al.*, 1993a). Quality assurance results were generally acceptable, although most field and analytical spike recoveries were greater than 100% for both compounds, and methidathion oxon was detected in blank samples (including laboratory blanks), suggesting matrix interference. A follow-up report on the overall sampling program attributed the elevated background in analysis of methidathion oxon to the electron-capture detector used (Royce *et al.*, 1993b). Methidathion oxon was corrected for this background, by subtracting 0.13 µg from each sample. Reporting limits were also high, probably because of the non-specific detector. For this reason, concentrations in this EAD are reported if greater than the limit of detection (LOD) instead of the limit of quantification (LOQ).

Both methidathion and its oxidation product, methidathion oxon, were detected at all sampling stations. Table 4 presents results for both analytes. In Table 4, samples below the limit of detection (LOD) were reported as  $\frac{1}{2}$  LOD. The LOD for methidathion was 0.01  $\mu g/m^3$ , and the LOD for methidathion oxon was 0.03  $\mu g/m^3$ . The reported values for samples below the LOD were 0.005  $\mu g/m^3$  and 0.015  $\mu g/m^3$ , respectively.

Reported methidathion concentrations ranged from below the LOD to  $0.56 \,\mu\text{g/m}^3$ , and the oxon concentrations ranged from below the LOD to  $0.098 \,\mu\text{g/m}^3$  (Table 4). Whether applications actually occurred near the sampling sites during the sampling interval was not reported by Royce *et al.* (1993a); however, ARB practice was to confirm that applications occurred within 1 mile of the monitoring sites when most or all ambient air samples for an AI or its breakdown product were below the LOQ (Baker *et al.*, 1996). Including samples collected at Site B, methidathion concentrations were below the LOQ in 91% of the samples (LOQ =  $0.03 \,\mu\text{g/m}^3$ ), and methidathion oxon concentrations were below the LOQ in 97% of the samples (LOQ =  $0.09 \,\mu\text{g/m}^3$ ).

In May through October 1994, Aston and Seiber (1997) monitored atmospheric concentrations of methidathion, methidathion oxon, chlorpyrifos, and chlorpyrifos oxon at three sites in Tulare County. Elevations of the sample stations were provided as the study was intended to monitor up-slope movement of pesticides used in the Central Valley into the Sierra Nevada Mountains. The first site was at the University of California Lindcove Field Station (previously identified as Site UC), at a reported elevation of 114 m above sea level. These data can be compared to those reported at Site UC by Royce et al. (1993a). The other two sites were in the Sierra Mountains, on Ash Mountain (Site AM, elevation 553 m) and Kaweah (Site K, elevation 1920 m). Site UC is surrounded by citrus groves, while Site AM was about 22 km east of the nearest known agricultural spraying location and Site K is 10 km northeast of Site AM (Aston and Seiber, 1997). Duplicate 24-hour air samples were collected at each site, at intervals of two to four weeks. Samplers were positioned 1 m above ground. Each air sampler consisted of a stainless steel tubes with 100-mesh screens on either end (which allow passage of particles with diameters up to approximately 149 μm), containing 150 ml of pre-cleaned XAD-4 resin and connected to a flowmeter and a high flow sampling pump with nominal flow rate of 700 L/min. Quality assurance consisted of duplicate samples and spikes (backup traps with resin were used with each spike to check for breakthrough), through which air was drawn for 24 hr at a flow rate of 620 L/min. Separate samplers were spiked with methidathion and methidathion oxon (0.05 µg of

each compound), so that conversion of methidathion to its oxon in a 24-hr sample could be estimated. Recovery of methidathion spikes totaled 88% (mean  $\pm$  standard deviation:  $59 \pm 14\%$  as methidathion, and  $28 \pm 0.13\%$  as methidathion oxon, for a mean 32% conversion); mean recovery of methidathion oxon spikes was  $75 \pm 12\%$ .

Table 4. Methidathion Concentrations in Ambient Air Monitoring in 1991 a

Date	Sit	e S <sup>b</sup>	Sit	te J	Site	e E	Site	UC	Sit	e B
	MT <sup>c</sup>	$MO^{c}$	MT	MO	MT	MO	MT	MO	MT	МО
June 27	0.027	0.015	0.032	0.015	0.019	0.015	0.014	0.048	0.005	0.015
July 1	0.024	0.038	0.018	0.015	0.005	0.015	0.005	0.033	0.013	0.015
July 2	0.005	0.047	0.018	0.087	0.028	0.097	0.005	0.040	0.012	0.044
July 3	0.005	0.015	0.012	0.015	0.012	0.015	0.005	0.015	0.005	0.015
July 4	0.005	0.015	0.011	0.015	NS d	NS	NS	NS	0.005	0.038
July 8	0.005	0.044	0.005	0.039	0.005	0.015	0.005	0.015	0.005	0.015
July 9	0.005	0.061	0.005	0.037	0.005	0.015	0.005	0.055	0.005	0.033
July 10	0.005	0.034	0.56	0.081	0.005	0.015	0.005	0.015	0.005	0.045
July 11	0.005	0.015	0.30	0.050	0.005	0.033	NS	NS	0.005	0.015
July 15	0.005	0.015	0.036	0.015	0.013	0.015	0.005	0.015	0.005	0.015
July 16	0.005	0.015	0.023	0.015	0.005	0.015	0.010	0.015	0.005	0.015
July 17	0.005	0.015	0.036	0.015	0.005	0.015	0.005	0.015	0.005	0.015
July 18	0.005	0.015	0.031	0.015	0.070	0.015	0.014	0.015	0.005	0.015
July 22	0.005	0.015	0.028	0.015	0.017	0.015	0.005	0.015	0.005	0.015
July 23	0.005	0.015	0.025	0.015	0.005	0.015	0.005	0.015	0.005	0.015
July 24	0.005	0.015	0.015	0.015	0.005	0.043	0.005	0.015	0.005	0.063
July 25	0.005	0.069	0.014	0.087	0.005	0.098	0.008	0.015	0.005	0.088
Mean <sup>e</sup>	0.011	0.027	0.069	0.032	0.013	0.028	0.007	0.023	0.006	0.028
SD <sup>e</sup>	0.009	0.018	0.144	0.027	0.017	0.028	0.003	0.014	0.002	0.021

<sup>&</sup>lt;sup>a</sup> Monitoring at sites in Tulare County (Royce *et al.*, 1993a). Concentrations are reported in μg/m³, and have not been corrected for recoveries. Methidathion oxon concentrations were corrected for a blank of 0.13 μg/sample. For results below the limit of detection (LOD), ½ LOD was reported; these values are italicized. LOD for methidathion: 0.01 μg/m³. LOD for methidathion oxon: 0.03 μg/m³. Results above the limit of quantification (LOQ) are shown in bold. LOQ for methidathion: 0.03 μg/m³. LOQ for methidathion oxon: 0.09 μg/m³.

Results from monitoring conducted by Aston and Seiber (1997) are presented in Table 5. Each value in Table 5 is the mean result of the duplicate samples. In cases where the difference between duplicate samples was >100%, Aston and Seiber (1997) did not report results, instead

<sup>&</sup>lt;sup>b</sup> Site S: Sunnyside Union Elementary School, Strathmore. Site J: Jefferson Elementary School, Lindsay. Site E: Exeter Union High School, Exeter. Site UC: University of California Lindcove Field Station, Exeter. Site B: background site at the ARB Ambient Air Monitoring Station, Visalia.

<sup>&</sup>lt;sup>c</sup> MT: Methidathion. MO: Methidathion oxon.

<sup>&</sup>lt;sup>d</sup> NS: No sample on this date.

<sup>&</sup>lt;sup>e</sup> Arithmetic mean and standard deviation (SD).

labeling the results as "not quantified" (abbreviated as NQ in Table 5). This was the case for methidathion in most samples collected at Site AM, and for all but one sample collected at Site K. Also, no chromatogram peak was detected (abbreviated as ND in Table 5) for methidathion or methidathion oxon in two samples from Site AM and for methidathion oxon in five samples from Site K.

Comparing results from Table 4 to those in Table 5 suggests that at Site UC, greater concentrations of methidathion oxon were detected in monitoring conducted in 1991 than in 1994. In 1991, methidathion oxon concentrations exceeded  $0.03 \,\mu\text{g/m}^3$  in four samples collected at Site UC; the highest concentration, corrected for background as described in Table 4, was  $0.055 \,\mu\text{g/m}^3$  (Royce *et al.*, 1993). In contrast, in 1994 the highest reported methidathion oxon concentration was  $0.010 \,\mu\text{g/m}^3$  (Aston and Seiber, 1997). Differences were less pronounced for methidathion; the highest methidathion concentration detected at Site UC in 1991 was  $0.014 \,\mu\text{g/m}^3$ , while in 1994 the highest concentration was  $0.017 \,\mu\text{g/m}^3$ .

Table 5. Methidathion Concentrations in Ambient Air Monitoring in 1994 a

Date	Site UC <sup>b</sup>		Site	AM	Site K	
	$MT^{c}$	$MO^{c}$	MT	MO	MT	MO
May 26	0.015	0.010	(No sample)	(No sample)	(No sample)	(No sample)
June 6-7	0.011	0.0085	0.00023	0.00066	NQ	ND
June 20-21	0.0095	0.0082	NQ <sup>d</sup>	0.00059	NQ	0.00021
July 11-12	0.0011	0.0023	NQ	0.00021	NQ	0.000085
July 25-26	0.017	0.0093	ND <sup>e</sup>	0.000085	NQ	ND
August 8-9	0.0024	0.0021	NQ	NQ	NQ	ND
August 22-23	0.0004	0.001	NQ	ND	NQ	NQ
September 18-19	0.0027	0.0049	NQ	0.000085	NQ	ND
October 17-18	0.00058	0.00028	NQ	NQ	NQ	ND
Mean <sup>f</sup>	0.0066	0.0052	0.00023	0.00033	All samples NQ	0.00015
$SD^f$	0.0066	0.0039	(one sample)	0.00028	0.002	0.000088

<sup>&</sup>lt;sup>a</sup> Monitoring at sites in Tulare County (Aston and Seiber, 1997). Concentrations are reported in μg/m³, and have not been corrected for recoveries. For results below the limit of quantification (LOQ), ½ LOQ was reported; these values are italicized. LOQ for methidathion: 0.000085 μg/m³. LOQ for methidathion oxon: 0.00017 μg/m³.

Figure 1 summarizes monthly applications of methidathion in Tulare County in 1991 and 1994, years when ambient air monitoring was done. Figure 1 shows that the highest use of methidathion in Tulare County in 1991 occurred during June, and that little use occurred in

<sup>&</sup>lt;sup>b</sup> Site UC: University of California Lindcove Field Station, Exeter, 114 m elevation. Site AM: Ash Mountain in the Sequoia National Park, 553 m elevation. Site K: Kaweah in the Sequoia National Park, 1920 m elevation. Samplers were positioned 1 m above ground.

<sup>&</sup>lt;sup>c</sup> MT: Methidathion. MO: Methidathion oxon.

<sup>&</sup>lt;sup>d</sup> NQ: Not quantified because duplicate samples differed by > 100%; no result reported by Aston and Seiber (1997).

<sup>&</sup>lt;sup>e</sup> ND: No detected: no peak detected in chromatogram.

<sup>&</sup>lt;sup>f</sup> Arithmetic mean and standard deviation (SD). Site UC mean and SD for samples collected in June through July were  $0.010 \pm 0.0066 \,\mu\text{g/m}^3$  for methidathion and  $0.0071 \pm 0.0032 \,\mu\text{g/m}^3$  for methidathion oxon.

March, April, May, November and December. In 1994, highest use again occurred in June, and more 10,000 lbs were applied in January and May through July. Overall use of methidathion in Tulare County was higher in 1994 than in 1991; a total of 75,518 lbs was applied in 1991 and a total of 103,007 lbs was applied in 1994. This suggests that higher concentrations reported in 1991 monitoring might have been a result of the analytical methods used in 1991, although it is also possible that location or timing of applications in 1991 resulted in higher levels at the monitoring station than in 1994; additionally, atmospheric conditions at the time of sampling, such as wind speed, inversion heights, and turbulence, differed between sampling periods in 1991 and 1994.

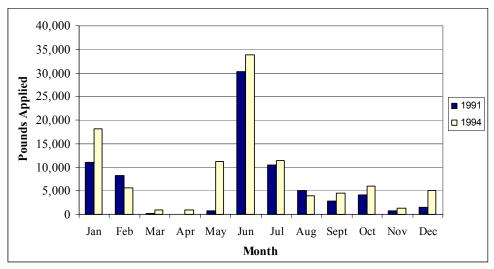


Figure 1. Pounds of Methidathion Applied in Tulare County in 1991 and 1994 a

In 1996 and 1997, the U.S.G.S. monitored atmospheric concentrations of several pesticides, including methidathion, at three locations in Sacramento County (Majewski and Baston, 2002). Two of the sites were rural, at airports northwest and southeast of Sacramento (samplers were about 3 m above ground); the third site was in downtown Sacramento (about 10 m above ground). The rural sites were approximately 10 and 20 miles (16 and 32 km) northwest and southeast, respectively, of the downtown site. Sample devices consisted of 119-cm<sup>3</sup> polyurethane foam plugs (mean density = 0.043 g/m<sup>3</sup>) in Teflon cartridges, connected to highvolume pumps with flow of approximately 100 L/min (Majewski and Baston, 2002). Weekly whole-air (particulates were not filtered out), composite samples were collected at each site throughout the study. Sampling was triggered when 15-min mean wind speeds were >1 m/sec in a northerly or southerly direction, and continued until the directional wind speed decreased below the trigger velocity; maximum sampling was 20 min/hr. Methidathion was detected just once at each of the rural sites (concentrations: 0.00035 and 0.00026 µg/m<sup>3</sup>); both samples were collected in January, and when the wind was from the south. Methidathion was not detected in samples collected from the downtown Sacramento site (reporting level 0.00020 µg/m<sup>3</sup>).

<sup>&</sup>lt;sup>a</sup> Pounds applied by all methods to all crops in Tulare County (DPR 2006b; queried May 25, 2006).

#### **Application Site Air**

Monitoring of methidathion concentrations in air was done in conjunction with an airblast application. An airblast sprayer uses a blower and high-pressure nozzles to apply liquids in a high-velocity, high-volume stream of air that can penetrate the foliage in orchard and vineyard crops. The sprayer is towed behind a vehicle driven by the applicator.

Application site monitoring occurred July 10-12, 1991; air samples were collected before, during, and 46.5 hours following airblast application of methidathion to a 15-acre orange grove in Tulare County (Royce *et al.*, 1993a). The application rate was not specified by Royce *et al.* (1993a), and information available elsewhere reports two possible rates for this study. In a summary of air monitoring prepared by DPR, the application rate was reported to be 1.5 lbs AI/acre (Kollman, 1995). However, in DPR's Pesticide Use Report (PUR) database the only 15-acre application to oranges in Tulare County on those dates reported an application rate of 3.0 lbs AI/acre (DPR, 2005b). This rate was used in this EAD.

Three air monitoring stations were located approximately 25 m north, approximately 15 m southeast, and approximately 150 m southeast of the orchard (prevailing winds in the area are typically from the northwest). Unfortunately, during the application and for several hours afterward, prevailing winds were from the southwest rather than the northwest (see Table 6), and no samplers were positioned to collect the airborne chemical concentrations anticipated to be highest.

Sample devices consisted of a glass tube containing two sections of XAD-2 resin (a 400-mg primary and 200-mg backup section) connected to a flowmeter and sampling pump with Teflon tubing; two resin tubes and flowmeters were connected to a low flow sampling pump with nominal flow rate of 1.85 L/min (Royce *et al.*, 1993a). Both methidathion and methidathion oxon were detected in the application monitoring samples. However, methidathion was below the LOD in 39% (7 of 18) of the application monitoring samples (LOD = 0.1  $\mu$ g/sample), and methidathion oxon was below the LOD in 72% (13 of 18) of the samples (LOD = 0.25  $\mu$ g/sample). In the first 24 hours, all samples were below the LOD for methidathion oxon.

Table 6 summarizes air concentrations during the monitoring periods. A time-weighted average (TWA) concentration was calculated for the first 24 hours, starting with the hour during which the application occurred (1:00 AM on July 11), and continuing through the sample collected from 3:00 to 9:30 PM on July 11 (i.e., samples 1 through 4; 20.5 hours of monitoring). This TWA value was used in estimating bystander exposures (see the Exposure Assessment section). Because of the detection of methidathion oxon in blanks, sample concentrations were corrected for a blank of  $0.13~\mu g/sample$  (the mean amount of methidathion oxon detected in blanks).

The highest methidathion concentrations occurred at the station 25 m north of the orchard; concentrations ranged from < LOD to 3.16  $\mu g/m^3$  (Table 6). At the station 15 m SE of the orchard, concentrations ranged from < LOD to 1.25  $\mu g/m^3$ . At the station 150 m SE of the orchard, methidathion concentrations ranged from < LOD to 0.28  $\mu g/m^3$ . Concentrations of methidathion oxon did not differ substantially between stations, ranging from < LOD to 0.18  $\mu g/m^3$ . Most samples were < LOD for methidathion oxon; because the LOD was determined on

a per-sample basis, the 24-hour TWA for methidathion oxon was slightly greater than the highest detected concentration at all three stations.

Table 6. Methidathion Concentrations Near an Orange Grove Receiving an Application <sup>a</sup>

Date and time of	North <sup>b</sup>		SE 1 <sup>b</sup>		SE 2 <sup>b</sup>		Wind	Wind
monitoring	MT <sup>c</sup>	$MO^{c}$	MT	MO	MT	MO	Speed <sup>d</sup>	Direction
July 10, 1991, 1500-1600 <sup>e</sup>	< LOD f	< LOD	< LOD	< LOD	< LOD	< LOD	5	NW
July 10-11, 2330-0900 g	0.33	< LOD	< LOD	< LOD	< LOD	< LOD	1	SW
July 11, 0900-1100	0.86	< LOD	< LOD	< LOD	< LOD	< LOD	4	SW
July 11, 1100-1500	1.40	< LOD	< LOD	< LOD	< LOD	< LOD	4	W/SW
July 11, 1500-2130	0.82	0.16	1.25	0.18	0.28	0.16	3	NW
24-hour TWA <sup>h</sup>	0.75	$0.22^{i}$	0.43	0.22	0.12	0.22	NA	NA
July 11-12, 2130-0730	3.16	0.14	0.60	< LOD	0.10	< LOD	1	SW
July 12-13, 0730-0730	0.46	0.18	0.30	0.14	< LOD	< LOD	3	SW/NW/E/S

<sup>&</sup>lt;sup>a</sup> Concentrations reported as μg/m³. Data from Royce *et al.* (1993a). Concentrations are reported in μg/m³, and have not been corrected for recoveries. Methidathion oxon concentrations were corrected for a blank of 0.13 μg/sample.

#### Water

Methidathion residues have been detected during monitoring of surface waters (Kuvila and Foe, 1995; Ross *et al.*, 1996). Kuvila and Foe (1995) monitored concentrations of five OPs in the Sacramento and San Joaquin rivers in January and February 1993. The five pesticides, including methidathion, are used as dormant sprays and were anticipated to be applied during the monitoring period. In the Sacramento River, only diazinon and methidathion were detected after heavy February rainfall. The maximum concentration of methidathion measured was 0.212 μg/L (Kuvila and Foe, 1995). Methidathion was also detected in the San Joaquin River following rain events in January and February (diazinon and chlorpyrifos also were detected); the maximum concentration measured was 0.586 μg/L (Kuvila and Foe, 1995).

<sup>&</sup>lt;sup>b</sup> The North station was 25 m, Southeast (SE) 1 station was 15 m, and SE 2 station was 150 m from the orchard.

<sup>&</sup>lt;sup>c</sup> MT: Methidathion. MO: Methidathion oxon.

<sup>&</sup>lt;sup>d</sup> Wind speed in miles/hour. NA: not applicable.

<sup>&</sup>lt;sup>e</sup> Background air monitoring before application.

<sup>&</sup>lt;sup>f</sup> Below limit of detection (LOD =  $0.1 \mu g$ /sample for methidathion,  $0.25 \mu g$ /sample for methidathion oxon).

<sup>&</sup>lt;sup>g</sup> Air monitoring during application (0100 – 0900 hours). Subsequent measures are post-application.

<sup>&</sup>lt;sup>h</sup> Time-weighted average (TWA) concentration over first 24 hours, beginning with application at 1:00 AM and ending with the sample completed at 9:30 PM. Samples taken during the first 20.5 hours were used as an approximation for the 24-hour TWA. For < LOD samples, ½ LOD was used in calculations. Example calculation: TWA = [(0.33 μg/m³ x 8 hr) + (0.86 μg/m³ x 2 hr) + (1.40 μg/m³ x 4 hr) + (0.82 μg/m³ x 6.5 hr)]/(20.5 hr) = 0.75 μg/m³.

Because the LOD was determined on a per-sample basis, the values for < LOD samples in the 24-hour TWA calculation vary inversely with volume sampled. For example, the value used for a 2-hour sample that was < LOD is calculated by dividing ½ LOD by the volume sampled:  $[(0.125 \,\mu\text{g})/(0.22 \,\text{m}^3 \,\text{sampled}) = 0.57 \,\mu\text{g/m}^3$ . Thus, it is possible for the 24-hour TWA to exceed the highest reported value. Example calculation in which the highest reported concentration was  $0.16 \,\mu\text{g/m}^3$ : TWA =  $[(0.14 \,\mu\text{g/m}^3 \,\text{x} \,8 \,\text{hr}) + (0.57 \,\mu\text{g/m}^3 \,\text{x} \,2 \,\text{hr}) + (0.30 \,\mu\text{g/m}^3 \,\text{x} \,4 \,\text{hr}) + (0.16 \,\mu\text{g/m}^3 \,\text{x} \,6.5 \,\text{hr})]/(20.5 \,\text{hr}) = 0.22 \,\mu\text{g/m}^3$ .

Ross *et al.* (1996) monitored concentrations of OP and carbamate insecticides in the San Joaquin River during two consecutive winters in 1991-1992 and 1992-1993. Of 108 samples collected, 19% had detectable levels of methidathion; nearly all detections coincided with rain events. Concentrations ranged between 0.07 and 12.4 μg/L (Ross *et al.*, 1996).

#### **Dislodgeable Foliar Residues**

Dislodgeable foliar residue (DFR) is defined as the pesticide residue that can be removed from both sides of treated leaf surfaces using an aqueous surfactant. DFR is assumed to be the portion of an applied pesticide available for transfer to humans from leaf and other vegetative surfaces. Measurements of DFR can be used, along with an appropriate transfer factor, to estimate the amount of pesticide adhering to clothing and skin surfaces following entry into a previously treated field. The DFR is reported as residue per leaf area ( $\mu g/cm^2$ ). DFR studies were conducted following methidathion use on citrus, cotton, and alfalfa crops (Table 7). In the subsequent discussion, Day 0 refers to the day of application, Day 1 is the first post-application day, and subsequent post-application days are similarly identified. A general equation for calculating DFR at a given time is: DFR<sub>t</sub> = DFR<sub>0</sub> ×  $e^{-kt}$ , in which e is the natural logarithm base; k is the slope of the log-linear, first-order dissipation curve, with units of days<sup>-1</sup>; and t represents the time interval (days); an equivalent expression is ln (DFR<sub>t</sub>) = ln (DFR<sub>0</sub>) - kt (Dong *et al.*, 1992). The half-life is calculated with the following equation: T<sub>1/2</sub> = (ln 0.5)/k, where k is the slope of the log-linear regression and is expressed as days<sup>-1</sup>.

Hernandez *et al.* (1998) collected grab samples of DFR coinciding with worker reentry activities. Methidathion was detected in seven of 82 samples, at concentrations ranging from 0.003 to 0.014 µg/cm<sup>2</sup>. These samples were collected during weeding of artichokes, (two of two samples contained methidathion), harvest of navel oranges (three of 46 samples), and harvest of peaches (two of 34 samples). Hernandez *et al.* (1998) intended to provide general information about pesticide exposures to reentry workers, and application information generally was unavailable for these data. Because of this, these data could not be used for fieldworker exposure estimates.

DFR studies following methidathion applications were done under a variety of conditions, and resulted in a range of dislodgeable residues and residue dissipation half-lives (Table 7). All available data from DFR dissipation studies performed in the U.S. are reported in Table 7. Studies were evaluated for acceptability based on criteria described in Iwata *et al.* (1977) and U.S. EPA (1996); for example, each acceptable study was performed under climate conditions typical of California growing season; there were no rain events during the study; samples were collected for several days extending at least through the REI; replicate samples were collected; residues were dislodged from leaf surfaces with a detergent solution (rather than an organic solvent); and the application rate was at or below the maximum stated on the product label for the crop (although application rates might not affect the dissipation rate, the relationship has not been studied for methidathion). DFR values used in exposure estimates were back-calculated from equations generated from study data (Andrews, 2000). Table 7 contains measured initial DFR values reported in each study; these values can differ from the predicted DFR<sub>0</sub> value, which is simply the intercept of the log-linear regression.

A few of the studies monitored DFR of methidathion oxon in addition to methidathion (Thompson *et al.*, 1979; Maddy *et al.*, 1984a, 1984b). Dislodgeable residues of the oxon were generally one to two orders of magnitude lower than methidathion residues in these studies. Methidathion oxon was not analyzed in more recent studies, and therefore was not included in reentry exposure estimates. The effect of oxon residues on worker exposure is unknown.

Table 7. Dissipation of Methidathion on Various Crops and Locations <sup>a</sup>

			Application		
	7		rate	Initial DFR <sup>c</sup>	Half-Life
Crop	Formulation <sup>b</sup>	Location	(lb AI/acre)	$(\mu g/cm^2)$	(Days) d
Alfalfa <sup>e</sup>	EC	Arizona	1.0	1.45	1.0
Cotton <sup>f</sup>	EC	California	0.5	0.34	1.4
Cotton g	WP	California	1.0	1.62	2.8
Cotton <sup>g</sup>	WP	North Carolina	1.0	2.03	2.8
Cotton <sup>g</sup>	WP	Texas	1.0	2.86	1.5
Orange h	EC	California	2.5	1.45 <sup>i</sup>	3.0
Orange h	EC	California	4.7	1.36 <sup>i</sup>	4.4
Orange <sup>j</sup>	EC	California	3.75	0.56	1.6
Orange <sup>j</sup>	EC	California	7.50	1.10	1.5
Orange k	EC	Florida	1.1	0.29	7.5
Orange <sup>l</sup>	EC	California	10.0	2.80	2.7
Orange m	EC	California	1.87	$0.10^{h}$	10.2
Orange <sup>n</sup>	EC	California	1.5	0.93	5.6
Orange <sup>n</sup>	EC	California	1.0	0.54	5.6
Orange o	WP	California	5.0	2.55	4.3
Orange °	WP	California	5.0	2.24	6.4
Orange p	WP	Florida	5.0	2.28	$0.8^{p}$

<sup>&</sup>lt;sup>a</sup> Studies shown in bold were used in calculating reentry worker exposure estimates.

<sup>&</sup>lt;sup>b</sup> EC: emulsifiable concentrate; WP: wettable powder. All formulations were mixed with water.

<sup>&</sup>lt;sup>c</sup> Measured on Day 0 (day of application), unless indicated otherwise.

<sup>&</sup>lt;sup>d</sup> Half-life calculated from the following equation:  $T_{1/2} = (\ln 0.5)/k$ , where k is the slope of the linear regression generated from study data:  $\ln (DFR_1) = \ln (DFR_0) - kt (Dong et al., 1992)$ .

<sup>&</sup>lt;sup>e</sup> Hensley (1981a); application with tractor-driven ground boom sprayer.

f Hensley (1981c); aerial application.

Rosenheck (1998b); Data following third application with tractor-driven ground boom sprayer. Equation used to calculate DFR for worker exposure estimate on Day t:  $\ln (DFR_t) = 0.653 \ln(\mu g/cm^2) - (0.429/day) t$  ( $r^2 = 0.867$ ).

<sup>&</sup>lt;sup>h</sup> Maddy (1976); application method not reported.

<sup>&</sup>lt;sup>i</sup> Measured on Day 1 (first day post-application), rather than on Day 0.

<sup>&</sup>lt;sup>j</sup> Iwata *et al.* (1979); application with ground boom sprayer.

<sup>&</sup>lt;sup>k</sup> Thompson *et al.* (1979); study conducted during rainy season; handgun application.

<sup>&</sup>lt;sup>1</sup> Hensley (1981b); first application with boom sprayer, second with speed sprayer.

<sup>&</sup>lt;sup>m</sup> Maddy (1984a); application method not reported.

<sup>&</sup>lt;sup>n</sup> Maddy (1984b); application method not reported.

<sup>&</sup>lt;sup>o</sup> Rosenheck (1998a); Data following second airblast application. Equation used to calculate DFR for worker exposure estimate on Day t:  $\ln (DFR_1) = 0.0462 \ln(\mu g/cm^2) - (0.108/day) t$  ( $r^2 = 0.986$ ).

<sup>&</sup>lt;sup>p</sup> Heavy rainfall followed second application.

#### **Cotton and Other Row Crops**

Two studies performed in California estimated DFR of methidathion following applications to cotton. In the first study, methidathion in the EC formulation was aerially applied at 0.5 lbs AI/acre (Hensley, 1981c). Measured DFR was 0.34  $\mu g/cm^2$  at Day 0. DFR dissipated to non-detectable levels (< 0.008  $\mu g/cm^2$ ) after seven days. The estimated half-life was 1.4 days.

In the second study, three ground boom spray applications of methidathion in the WP formulation were done at the maximum label rate of 1.0 lb AI/acre (Rosenheck, 1998b). The measured DFR was  $1.62~\mu g/cm^2$  after the final application. DFR decreased to less than the detection limit (0.0096  $\mu g/cm^2$ ) 21 days later, with an estimated half-life of 2.8 days. Data from this study were used to estimate DFR in cotton in this EAD because the application rate (1.0 lb AI/acre) is the maximum label rate allowed in California. These data for DFR in cotton differ from those used by U.S. EPA (Travaglini, 1999), which were from studies done in North Carolina and Texas.

A log-linear regression model gives an equation for DFR dissipation of the form: DFR<sub>t</sub> = DFR<sub>0</sub> ×  $e^{-kt}$ . Based on data collected from the California study (Rosenheck, 1998b) the following values were determined for the constants: DFR<sub>0</sub> = 1.92 µg/cm² and k = 0.651/day ( $r^2$  = 0.867). The estimated dissipation half-life was 1.6 days. The resulting Equation 1, used to predict DFR values used in exposure estimates, is shown below. The DFR at Day 2 (DFR<sub>2</sub>) is of interest in the exposure assessment as the REI following application of methidathion to cotton is 48 hours, and by law, Day 2 is the earliest workers may enter without wearing protective clothing and PPE required for handlers. Using Equation 1, DFR<sub>2</sub> was estimated to be 0.815 µg/cm².

#### Equation 1. Calculation of Dislodgeable Foliar Residues on Cotton <sup>a</sup>

$$DFR_t = (1.92 \mu g / cm^2)(e^{(-0.651/day)t})$$
 or  $\ln(DFR_t) = 0.653 \ln(\mu g / cm^2) - (0.429/day)t$ 

As no DFR data were available for fieldworkers in artichokes or safflower, DFR data from cotton were substituted. The REI for both crops is 2 days; as with cotton, the Day 2 DFR (DFR<sub>2</sub>) was used in the exposure assessment for reentry tasks in these crops. Using Equation 1, DFR<sub>2</sub> was estimated to be  $0.815~\mu g/cm^2$ .

#### Citrus

Numerous DFR studies have been conducted following methidathion use on orange trees. Of the studies performed in California, two (Maddy, 1976; Iwata *et al.*, 1979) provided too few DFR measurements, resulting in inadequate data. Four acceptable studies were available.

In the first study, the EC formulation was applied by growers to two sites in Fresno County, at the rates of 1.5 and 1.0 lbs AI/acre (Maddy, 1984b). At 8 hours post-application, the average DFR was  $0.93 \,\mu \text{g/cm}^2$  at the first site and  $0.54 \,\mu \text{g/cm}^2$  at the second. Estimated half-lives were 5.6 days at both sites. The second study was similar to the first, except that methidathion was applied to a single orange grove at the rate of 1.87 lbs AI/acre (Maddy, 1984a). At 24 hours

<sup>&</sup>lt;sup>a</sup> DFR: Dislodgeable Foliar Residue. t: Days post-application.

post-application, the average DFR was  $0.097~\mu g/cm^2$ ; the estimated half-life was 10.2~days; and residues decayed to non-detectable levels (detection limit  $0.0005~\mu g/cm^2$ ) after 28 days.

In the third study, the EC formulation was applied at the elevated rate of 10 lbs AI/acre via ground boom sprayer and speed sprayers in Corona, California (Hensley, 1981b). The initial (Day 0) average DFR was 2.80  $\mu g/cm^2$ ; DFR decreased to 0.084  $\mu g/cm^2$  by Day 14. The estimated half-life was 2.7 days.

In the fourth study, two ground applications were done at the maximum label rate (5 lb AI/acre) of methidathion, using the WP formulation, at each of two sites in California (Rosenheck, 1998a). DFR declined rapidly over the 35-day monitoring period following the second application. The application rate monitored by Rosenheck (1998a) is the maximum label rate allowed in California (5.0 lb AI/acre); these were used in this document to estimate DFR in citrus. U.S. EPA used data from this same study (Travaglini, 1999). Rosenheck (1998a) monitored DFR at two sites in California, one in Madera County and one in Tulare County. Residues dissipated more slowly at the site in Tulare County, 6.4 days vs. 4.3 days at the site in Madera County (Table 7). A linear regression done on natural log-transformed data from the site in Tulare County monitored by Rosenheck (1998a) resulted in Equation 2 ( $r^2 = 0.937$ ). The REI for citrus is 30 days, and the Day 30 DFR (DFR<sub>30</sub>) was used in the acute exposure assessment for reentry tasks in citrus. Using Equation 2, DFR<sub>30</sub> was estimated to be 0.015  $\mu$ g/cm<sup>2</sup>.

#### Equation 2. Calculation of Dislodgeable Foliar Residues on Citrus <sup>a</sup>

 $\ln DFR_t = 0.667 \ln(\mu g / cm^2) - (0.162 / day)t$ 

<sup>a</sup> DFR: Dislodgeable Foliar Residue. t: Days post-application.

#### **Other Residues**

Post-application methidathion residues have been measured in and on fruit (Iwata et~al., 1979; Carmen et~al., 1981), as well as in soil (Iwata et~al., 1979). Measured dislodgeable surface residues on oranges following applications of 3.6 to 5.6 lbs AI/acre ranged from 0.5 to 1.1  $\mu g/cm^2$  on Day 0, and from 0.01 to 0.04  $\mu g/cm^2$  on Day 30 (Iwata et~al., 1979). Instead of dislodgeable surface residues, Carmen et~al. (1981) measured concentrations of methidathion in chopped orange rinds extracted with acetone; oranges were collected following methidathion applications of 3.9 lbs AI/acre. Fruit samples were initially collected on the first post-application day, and average concentrations in the rinds were between 0.5 and 1.1  $\mu g/g$  (Carmen et~al., 1981). Samples were collected on five additional occasions between Day 10 and Day 60, and methidathion concentrations in the rinds remained fairly constant. In contrast, methidathion concentrations in soil samples were below 0.01  $\mu g/g$  (Carmen et~al., 1981). Methidathion concentrations in soil samples collected by Iwata et~al. (1979) following applications of 3.6 to 5.6 lbs AI/acre ranged from 500  $\mu g/g$  immediately following application, to < 10  $\mu g/g$  on Day 30 (Iwata et~al., 1979). These residues on fruit and in soil may add to overall worker exposure; however, little information is available about non-foliar residues. Generally, such residues are

anticipated to have insignificant contributions to worker exposure when compared to DFR (Popendorf and Leffingwell, 1982), and were not considered further in the exposure assessment.

#### EXPOSURE ASSESSMENT

Occupational handler and reentry exposure estimates for significant exposure scenarios are discussed in this section; these estimates are based on exposure monitoring with surrogate chemicals and, in the case of reentry exposure, on studies of chemical-specific residues on foliage. Estimates of public exposure to airborne methidathion are also presented; these estimates are based on air monitoring of methidathion at an application site (bystander) and ambient air monitoring, along with default inhalation rates. Foliar residue and air monitoring data were described in the Environmental Concentrations section. Assumptions and defaults incorporated into exposure estimates are described in this section, along with calculations of the estimates.

DPR considers short-term (or acute) exposure to be any exposure that persists for seven days or less. The acute exposure typically estimated by DPR for occupational scenarios is the amount received in one full workday; unless otherwise stated, this is assumed to be 8 hours. Acute bystander and ambient air exposures state the dosage received in a 24-hour day. Acute exposure estimates are important because, while an organism can generally tolerate a higher exposure for a short period than it can for a longer period, some adverse effects can be produced in a short period of time if the exposure is sufficient.

Handler and reentry worker exposure monitoring studies typically monitor individuals for one day or less. Studies are evaluated for acceptability according to whether monitored tasks are adequately described and performed as in the field, study conditions mimic ones actually encountered, analytical methods and quality assurance are acceptable, and enough individuals were monitored. Properly-conducted studies allow estimation of characteristics of the exposure distribution, including basic statistics such as mean and standard deviation.

Higher-than-average daily exposures do, by definition, occur in every group monitored. Although it may be appropriate (absent evidence to the contrary) to assume average daily exposures over the long term, for acute exposures this assumption is not appropriate. By legislative mandate, DPR has an obligation to protect any individual exposed to pesticides as a result of legal uses (CFAC 12824). Protecting only those exposed at the "average" level would allow many individuals (anyone with above-average exposure) to be exposed to potentially acutely toxic concentrations. DPR therefore uses an upper-bound estimate of acute exposure.

The upper-bound value that DPR generally uses for short-term exposure is the estimated 95<sup>th</sup> percentile of the distribution of daily exposures. DPR assumes that this distribution can be approximated by a lognormal distribution. The 95<sup>th</sup> percentile is the value such that 95% of anticipated exposures would be lower and 5% would be higher. The estimate of the 95<sup>th</sup> percentile of a lognormal distribution is  $\exp\{\hat{\mu} + Z_{0.95}\hat{\sigma}\}$ , where  $\hat{\mu}$  and  $\hat{\sigma}$  are the estimated mean and standard deviation of the natural logs of exposure and  $Z_{0.95} = 1.645$ .

As explained by Powell (2002), DPR's concern is for the highest exposure an individual may realistically experience that is associated with legally-permitted uses (such as while performing a label-permitted activity). However, DPR estimates the 95<sup>th</sup> percentile of daily exposure rather than the maximum, because exposures are assumed to follow a lognormal distribution, which in theory has an infinitely large maximum. In practice of course, exposures must have a finite maximum value because a finite amount of active ingredient is applied. DPR uses the 95<sup>th</sup> percentile rather than a higher percentile (e.g., 99<sup>th</sup> percentile), because the higher a percentile, the less reliably it can be estimated (i.e., the error associated with the estimate becomes larger). Also, DPR recognizes that the assumed lognormal distribution may not exactly match the actual distribution of exposure values, and that any discrepancy from the lognormal distribution will be greatest at the upper extremes (Ott, 1990). DPR believes that the 95<sup>th</sup> percentile is a realistic estimate of the highest exposures.

To estimate intermediate- and longer-term exposures, the average daily exposure is of interest because over these periods of time, a worker is expected to encounter a range of daily exposures (i.e., DPR assumes that with increased exposure duration, repeated daily exposure at the upper-bound level is unlikely). To estimate the average, DPR uses the arithmetic mean of daily exposure. The arithmetic mean is used rather than the geometric mean or the median because, although it can be argued that geometric means better indicate the location of the center of a skewed distribution, it is not the center that is of interest in exposure assessment, but the expected magnitude of the long-term exposure. While extremely high daily exposures are low-probability events, they do occur, and the arithmetic mean appropriately gives them weight in proportion to their probability. (In contrast, the geometric mean gives decreasing weight as the value of the exposure increases, and the median gives no weight whatsoever to extreme exposures.) In most instances, the mean daily exposure of individuals over time is not known. However, the mean daily exposure of a group of persons observed in a short-term study is believed to be the best available estimate of the mean for an individual over a longer period.

#### **Handlers**

#### **Exposure Monitoring**

Several studies are available in which worker exposure to methidathion during handling was evaluated. Most of these studies involved applications to three crops, alfalfa, cotton, and citrus. None of these studies was acceptable, for reasons described below. Additionally, a single airblast application of methidathion to almonds was monitored (Wang *et al.*, 1987). However, the individual monitored in this study spilled methidathion during open pouring (a practice not allowed under existing laws), invalidating even limited use of data collected in this study for exposure assessment. Also, in a large monitoring study (Drevenker *et al.*, 1991), workers applying three OP insecticides, including methidathion, were monitored using serum paraoxonase and arylesterase activities and urine analysis for several dialkylphosphorus metabolites. The study was not designed to monitor exposure to any particular insecticide, and was not used in this exposure assessment.

A study of exposure during methidathion applications to alfalfa was performed in Arizona (Hensley, 1981a). The study site consisted of two 4-acre plots to which the EC methidathion

formulation was applied using a ten-foot spray boom. One mixer/loader (M/L) and one applicator was involved in the application to each plot, with one M/L using a closed system and the other doing an open-pour mix/load. Methidathion was applied 1.0 lb AI/acre in 20 gallons of water (i.e., a total of 4.0 lbs AI was handled by each individual). Both M/L operations took about 15 minutes; the applicator exposures were 2 hours 9 minutes and 2 hours 31 minutes. Extrapolating the measured results to an 8-hour day with an assumption that exposure was constant for the full workday (e.g., for M/L, results were multiplied by [8 hr]/[0.25 hr] = 32), the estimate for the M/L in the open system was 140  $\mu$ g/person/day (4.2  $\mu$ g/lb AI handled); for M/L using the closed system, 330  $\mu$ g/person/day (10  $\mu$ g/lb AI handled); and for applicators, 1200  $\mu$ g/person/day (38  $\mu$ g/lb AI handled). The higher exposure to M/L working with a closed system was unexpected, and possibly was due to a spill on the hands (Hensley, 1981a). This study was unacceptable because of limited replication and short exposure durations, 15 minutes for M/L and 2 hours for applicators.

Handler exposure was measured during aerial applications to cotton of the EC methidathion formulation at the rate of 0.5 lb AI/acre to a site in El Centro, California (Hensley, 1981c). Applications were made to 20 acres containing 5-foot tall cotton plants, flying 5-8 feet above the canopy; a total of 10 lb AI was handled by each of three workers (a mixer/loader, an applicator, and a flagger). The single application took approximately 10 minutes; although the mixing and loading times were not stated, they also are anticipated to be short. Estimated exposures were extrapolated to a full day, based on measurements made from this unreplicated study. Estimated exposures were 3.0, 2.7, and 2.3  $\mu$ g of methidathion/day for applicators, M/L, and flaggers, respectively (0.038, 0.034, and 0.029  $\mu$ g/lb AI handled). Three scouts entered the field on post-application Day 1 and Day 3, making three 6-minute trips into the field each time. Scouts were estimated to have exposures of 170 (Day 1) and 9.2 (Day 3)  $\mu$ g of methidathion/day. This study was unacceptable because of limited replication and short exposure durations.

Three studies monitored worker exposure during methidathion application to citrus (Hensley, 1981b; Maddy *et al.*, 1983; Krieger *et al.*, 1998). In the first study, worker exposure was measured during application of the EC formulation at 10 lbs AI/acre (Hensley, 1981b). One acre was treated by a tractor-mounted boom sprayer (a total of 10 lb AI was applied) and three acres by airblast application in 2000 gallons of water (a total of 30 lb AI was applied). Two M/L working for 55 and 130 minutes, and two applicators working for 195 and 200 minutes, were evaluated for potential exposure with patches placed on their work clothing. Exposures were estimated as 210 and 1300 μg/person/day for M/L (2.6 and 5.4 μg/lb AI handled) and 3900 and 8700 μg/person/day for applicators (48 and 36 μg/lb AI handled). No detectable levels of methidathion or of two metabolites occurred in worker urine (the detection limit for all three substances was 0.01 mg/L). The third urinary metabolite, S-2,3-dihydro-5-methoxy-2-oxo-1,3,4-thiadiazole, was found in each M/L in small quantities (0.04 and 0.06 ppm) at 12 and 24 hours. This study was unacceptable because of limited replication and short exposure durations.

In the second citrus study, exposure monitoring was done on one individual loading and applying a pesticide mixture containing Supracide 2E at the rate of 3 lbs AI/acre (Maddy *et al.*, 1983). The study was unacceptable because of inadequate replication (one replicate). Also, the application equipment used consisted of a specially designed oscillating boom sprayer, and its

relevance to equipment that is typically used is unknown. Finally, pre-application samples showed high background methidathion residues, invalidating data collected during application.

The third citrus study was designed to compare exposure differences between two types of protective suits (Krieger *et al.*, 1998). Two applications of a WP formulation were made by mixer/loader/applicators (M/L/A) using airblast sprayers at a rate of 2.0 lbs AI/acre. Absorption of methidathion was estimated by analysis of collected urine for six dialkyl phosphates that are common metabolites of organophosphates. Methidathion itself was not measured, nor were important metabolites, such as sulfoxide and desmethyl methidathion, identified in animal metabolism studies (Chopade and Dauterman, 1981; Szolics, 1987). Thus, although relative methidathion exposure between workers using the two types of protective suits could be determined, this study was not designed to provide data for exposure assessments. This study was also unacceptable because of inadequate replication.

#### **Exposure Estimates Using Surrogate Data**

As no acceptable studies were available for assessment of handler exposure, estimates were derived using the Pesticide Handler Exposure Database, or PHED (PHED, 1995). PHED was developed by the U.S. EPA, Health Canada and the American Crop Protection Association to provide non-chemical-specific exposure estimates for specific handler scenarios. The use of non-chemical-specific exposure estimates is based on the assumption that exposure is a function of the work activity, application method, pesticide formulation and the amount of active ingredient handled, and not of the physical-chemical properties of the specific active ingredient (Versar, 1992). PHED combines exposure data from multiple monitoring studies of different active ingredients. The user selects a subset of the data having the same work activity and the same application method and formulation as the target scenario; PHED then calculates and reports the average exposure for this subset.

Because PHED reports only average exposures, and because estimating the 95<sup>th</sup> percentile requires also knowing the standard deviation, it is not possible to calculate the 95<sup>th</sup> percentile upper-bound estimate of short-term exposure using PHED output alone. However, if it assumed that exposures can be approximated by a lognormal distribution and that they have a coefficient of variation of 100%, the 95<sup>th</sup> percentile upper-bound estimate can be calculated (the calculation will be presented shortly). The coefficient of variation is the ratio of the standard deviation to the mean expressed as a percentage. A coefficient of variation of 100% occurs when the standard deviation and the mean are equal. In a normal distribution, it would be unusual to see such a large standard deviation, but in lognormal distributions it is not at all uncommon.

PHED has many sources of uncertainty. First, estimates from PHED combine measurements from diverse studies involving different protocols, analytical methods and residue detection limits. Second, most dermal exposure studies in PHED use the patch dosimetry method of Durham and Wolfe (1962); residues on patches placed on different parts of the body are multiplied by the surface area of the body part to estimate its exposure. These partial estimates are then summed to provide a total body exposure estimate. Some studies observed exposure to only selected body parts such as the hands, arms and face. As a consequence, dermal exposure estimates for different body parts may be based on a different set of observations. Third, for

some handler scenarios, the number of matching observations in the PHED is so small that the possibility they do not represent the target scenario is substantial. There is uncertainty inherent in any estimate based on data. DPR believes that additional uncertainty is introduced by using PHED data, whose relevance to a target scenario usually cannot be fully assessed due to incomplete information about the application equipment and other aspects of the scenario. Due to the degree of uncertainty introduced by PHED, DPR calculates upper confidence limits (UCL) on the exposure statistics to increase the confidence in the estimates of exposure. When estimating long-term exposure using PHED, DPR uses the 90% UCL on the arithmetic mean. When estimating short-term exposure using PHED, DPR uses the 90% UCL on the 95<sup>th</sup> percentile. Confidence limits on percentiles are described in Hahn and Meeker (1991; Section 4.6).

PHED reports the mean of total dermal exposure, but only the coefficients of variation for separate body regions. Because the sample sizes per body region differ and because the correlations among body regions are unknown, the standard deviation of total dermal exposure cannot be calculated. However, the two assumptions previously mentioned, that exposures can be approximated by a lognormal distribution and that they have a coefficient of variation of 100%, allow an approximation to the UCL (Powell, 2002). Under this approximation, the 90-percent UCL for the 95<sup>th</sup> percentile of a lognormal distribution is

$$\exp\left\{\hat{\mu}+g'(0.90;0.95;n)\cdot\hat{\sigma}\right\}.$$

The symbols  $\hat{\mu}$  and  $\hat{\sigma}$  represent the arithmetic mean and standard deviation of the natural logarithms of the data. Values of the multiplier  $g'_{(1-\alpha,\,p,\,n)}$ , which depend on the confidence level  $(1-\alpha)$ , the percentile (p) and the sample size (n), are tabled in Hahn and Meeker (1991; Table A12.d). It is not possible to calculate the UCL using the formula above because the arithmetic mean of the natural logarithms is unavailable from PHED. (The value of the standard deviation of the logarithms derives from the assumed coefficient of variation of 100%.) However, it can be shown (Powell, 2002) that the estimated UCL is simply a multiple of the arithmetic mean of (non-log-transformed) exposure, which is available from PHED. Similarly, the 90% UCL for the mean is

$$\exp\left\{\hat{\mu}+\frac{1}{2}\hat{\sigma}^2+\frac{\hat{\sigma}}{\sqrt{n-1}}\cdot C(\hat{\sigma};n-1;1-\alpha)\right\},\,$$

where the values of *C* are tabled in Land (1975) and can also be obtained from a computer program written by Land *et al.* (1987). This formula also reduces to a multiple of the arithmetic mean exposure. The values of these multiples, for different sample sizes (n), are tabled in Powell (2002). DPR calculates the UCL for both the 95<sup>th</sup> percentile and the mean by multiplying arithmetic mean exposure by rounded values of the multipliers (Tables 2 and 4, Powell, 2002). PHED data used in estimating handler exposure are summarized in Table 8.

#### **Protection Factors**

As explained in the Label Precautions section, handlers are required to wear protective clothing and equipment specified on product labels, unless exempted under regulation. Regulations also can require additional PPE in some cases. In this EAD, 90% protection factors are applied for handlers legally required to wear gloves or respirators. The protection factors are based on studies suggesting that hand exposures are decreased by approximately an order of magnitude when handlers wear gloves (Aprea *et al.*, 1994), and that inhalation exposure is decreased by approximately an order of magnitude when handlers wear respirators (NIOSH, 1987).

Table 8. Data Used in Estimates of Pesticide Handler Exposure

			rt-term Expos			-Term Expos			
W 1 T 1	<b>A</b> a	<u>(μ</u>	(µg/lb AI handled)			(µg/lb AI handled)			
Work Task	App. <sup>a</sup>	Dermal	Inhalation	Total <sup>c</sup>	Dermal	Inhalation	Total <sup>c</sup>		
<u>Aerial</u>									
$M/L^{d}$	1	91.8	0.138	46.0	36.6	0.055	18.4		
Applicator	3	371	0.286	186	124	0.115	62.1		
Flagger	4	152	0.080	76.1	38.0	0.020	19.0		
Airblast									
M/L	1	91.8	0.138	46.0	36.6	0.055	18.4		
Applicator	5	4,090	2.16	2,050	1,020	0.541	511		
Groundboom									
M/L	1	91.8	0.138	46.0	36.6	0.055	18.4		
Applicator	6	102	0.472	51.5	25.5	0.118	12.9		
Backpack spra	yer								
M/L/A d	7	134,000	10.5	67,000	44,600	3.51	22,300		
Low-pressure l	Low-pressure handwand								
M/L/A l	8	9,480	13.7	4,750	3,160	4.56	1,580		

<sup>&</sup>lt;sup>a</sup> Appendix number for Pesticide Handlers Exposure Database (PHED) subset details.

For example, if hand exposure is  $5.97 \mu g/lb$  AI handled when a handler is not wearing gloves, then hand exposure for the handler wearing gloves is calculated as follows:

Exposure adjustment: 1.0 - 0.9 = 0.1

Exposure estimate:  $(5.97 \mu g/lb \text{ AI handled}) \times (0.1) = 0.597 \mu g/lb \text{ AI handled}$ 

#### **Aerial Applications**

Aerial application exposure estimates assumed a closed system for M/L and that handlers (M/L, applicators and flaggers) were the clothing and PPE listed on product labels (see California

<sup>&</sup>lt;sup>b</sup> Calculated from surrogate data using PHED database and software (PHED, 1995). Appropriate protection factors were applied as explained in the text and listed in Appendices 1-8.

<sup>&</sup>lt;sup>c</sup> Total Exposure ( $\mu$ g/lb AI handled) = [(dermal exposure)(0.5) + (inhalation exposure)(1.0)]

 $<sup>^{</sup>d}$  M/L = mixer/loader. M/L/A = mixer/loader/applicator.

Requirements section); this included long-sleeved shirt and pants, shoes plus socks, waterproof gloves, and a respirator. Aerial applicators (pilots) are not required to wear gloves during an application (3 CCR 6738), and were not assumed to wear gloves (see Appendix 3). Open cockpits were assumed for pilots, as there is no requirement for closed cockpits during applications.

As handling of WP products in WSP resulted in higher exposure estimates than handling of EC products in a closed system (compare Appendices 1 and 2), use of WP products was assumed. In estimating exposure of M/L handling liquid products, the PHED data set was generated using data from studies in which respirators were not used (Appendix 1), and a 90% protection factor was applied to the data set for use of a respirator (NIOSH, 1987). The same protection factor was applied to PHED results for pilots (Appendix 3). Two protection factors were applied to PHED results for flaggers (Appendix 4): a 90% protection factor was applied to hand exposure for use of gloves (Aprea *et al.*, 1994), and a 90% protection factor was applied to inhalation exposure for use of a respirator (NIOSH, 1987). The protection factor for gloves was needed because the flagger PHED scenario with gloves gave results with insufficient numbers of high-quality observations, and the scenario used did not include gloves. Unlike pilots, flaggers are not exempted from wearing gloves under California regulation (3 CCR 6738).

Acute exposures were estimated using upper bound values as described above; estimates are summarized in Table 9. The acute exposure estimates were 1.15 mg/kg/day for M/L, 4.65 mg/kg/day for aerial applicators, and 1.90 mg/kg/day for flaggers. The corresponding ADDs estimated by U.S. EPA for workers wearing long-sleeved shirts, long pants, shoes and socks, and using respirators, were 0.251 mg/kg/day for M/L, 0.132 mg/kg/day for aerial applicators (pilots), and 0.302 mg/kg/day for flaggers (Travaglini, 1999).

To estimate intermediate and long-term exposures of workers involved in aerial applications of methidathion, temporal patterns were investigated by examining PUR data for the five year period, 2000 to 2004 (DPR, 2006b). Numbers of sequential days with pesticide applications (and not more than two consecutive days in the interval without applications) were totaled for an estimate of seasonal exposure duration, and numbers of days per year were totaled for annual exposure estimates. In both cases, days were rounded to the nearest month, as stated below. Data from the six counties with the most aerial methidathion applications were examined. These counties were grouped regionally; i.e., counties within each group are adjacent, and between each group there are counties with little or no aerial methidathion application. Three county groups were examined, and of these groups Butte and Sutter counties are northernmost; San Joaquin County is central; and Fresno, Kings and Tulare counties are southernmost. Fresno, Kings, and Tulare counties had the most sequential days with pesticide applications, 17 (rounded to 1 month). The average days per year with pesticide applications in Fresno, Kings, and Tulare counties was 22 days per year (rounded to 1 month). Based on these data, seasonal and annual exposures were both estimated to occur over 1 month.

**Table 9. Estimates of Pesticide Handler Exposure to Methidathion** 

	Acute ADD <sup>a</sup>	SADD <sup>b</sup>	AADD <sup>c</sup>	$LADD^{d}$
Work Task	(mg/kg/day)	(mg/kg/day)	(mg/kg/day)	(mg/kg/day)
Aerial <sup>e</sup>				
$M/L^f$	1.15	0.460	0.038	0.020
Applicator	4.65	1.55	0.129	0.069
Flagger	1.90	0.475	0.040	0.021
<u>Airblast</u> <sup>g</sup>				
M/L	0.131	0.053	0.004	0.002
Applicator	5.86	1.46	0.122	0.065
Groundboom h				
M/L	0.158	0.063	0.011	0.006
Applicator	0.177	0.044	0.007	0.004
Backpack sprayer i				
$M/L/A^f$	0.191	NA	NA	NA
Low-pressure handwand <sup>j</sup>				
M/L/A	0.0034	NA	NA	NA

<sup>&</sup>lt;sup>a</sup> Acute Absorbed Daily Dosage (acute ADD) is an upper-bound estimate calculated from the short-term exposure estimate given in Table 8. Acres treated per day assumptions differed for each application method. Application rate is maximum rate on product labels, and differed for each application method. Body weight assumed to be 70 kg, based on mean for adult U.S. population (U.S. EPA, 1997). Calculation: Acute ADD = [(short-term exposure) x (acres/day) x (rate lb AI/acre)]/(70 kg body weight).

SADD =  $[(long-term\ exposure)\ x\ (acres/day)\ x\ (rate\ lb\ AI/acre)]/(70\ kg\ body\ weight)$ .

b Seasonal Average Daily Dosage is a 90% upper confidence estimate calculated from the long-term exposure estimate given in Table 8. SADD is the daily dose estimated for the season, based on recent use patterns. Acres treated per day assumptions differed for each application method. Application rate is maximum rate on product labels, and differed for each application method. Body weight assumed to be 70 kg, based on mean for adult U.S. population (U.S. EPA, 1997). Calculation:

<sup>&</sup>lt;sup>c</sup> Annual Average Daily Dosage = SADD x (annual use months per year)/(12 months in a year). Annual use estimates vary for each scenario.

<sup>&</sup>lt;sup>d</sup> Lifetime Average Daily Dosage = AADD x (40 years of work in a lifetime)/(75 years in a lifetime).

<sup>&</sup>lt;sup>e</sup> Estimate assumed a maximum application rate of 5 lb AI/acre. Assumed 350 acres treated/day (U.S. EPA, 2001). Estimated season for SADD is 1 month; estimated annual use is 1 month.

f M/L = mixer/loader. M/L/A = mixer/loader/applicator.

<sup>&</sup>lt;sup>g</sup> Estimate assumed a maximum application rate of 5 lb AI/acre. Assumed 40 acres treated/day (U.S. EPA, 2001). Seasonal and annual exposures are estimated to occur over 1 month.

<sup>&</sup>lt;sup>h</sup> Estimate assumed a maximum application rate of 3 lb AI/acre. Assumed 80 acres treated/day (U.S. EPA, 2001). Seasonal and annual exposures are estimated to occur over 2 months.

<sup>&</sup>lt;sup>1</sup> Estimated use: 40 gal/day, containing 0.5 lb AI/100 gal (U.S. EPA, 2002). Total: 0.2 lb AI/day. Seasonal and annual exposures are not anticipated to occur. NA = Not applicable.

<sup>&</sup>lt;sup>j</sup> Estimated use: 10 gal/day, containing 0.5 lb AI/100 gal (U.S. EPA, 2002). Total: 0.05 lb AI/day. Seasonal and annual exposures are not anticipated to occur.

#### **Ground Applications, Airblast**

Significant exposure scenarios involving airblast applications are M/L and applicator. Airblast M/L/A were assumed to have exposures in the range of M/L and applicators (exposure estimates are normalized to an 8-hour day, and M/L/A would mix/load part of the day, and apply for the remainder). All M/L exposure estimates (in support of aerial, airblast, and groundboom applications) used the same surrogate PHED data, with the same clothing and PPE assumptions, and the same protection factors were applied to the PHED results. These assumptions and protection factors were discussed above in the aerial applications section. Airblast applicators were assumed to use clothing and PPE listed on product labels, for reasons stated in the California Requirements section. Airblast applicator scenarios used open cabs, as there is no requirement for closed cabs. For the applicator exposure estimate (Appendix 5), a 90% protection factor was applied to the inhalation exposure result for use of a respirator (NIOSH, 1987).

The acute exposure estimates were 0.131 mg/kg/day for M/L and 5.86 mg/kg/day for airblast applicators. The corresponding ADD estimated by U.S. EPA for M/L wearing long-sleeved shirts, long pants, shoes and socks, and using respirators, was 0.028 mg/kg/day (Travaglini, 1999). For airblast applicators, U.S. EPA estimated an ADD of 0.68 mg/kg/day dermal (assumed long-sleeved shirts, long pants, shoes and socks) and 0.0026 mg/kg/day inhalation (assumed use of respirator), for a total ADD of 0.683 mg/kg/day (Travaglini, 1999).

Airblast applications are common in tree crops, and for the purpose of estimating handler exposure all ground applications to these crops were assumed to be airblast applications. Temporal patterns were investigated by examining the most recent five years of PUR data (2000 to 2004) in Kern County (DPR, 2006b). Numbers of sequential days with pesticide applications (and not more than two consecutive days in the interval without applications) were totaled for an estimate of seasonal exposure duration, and numbers of days per year were totaled for annual exposure estimates. Small applications, defined as < 20 acres/day, were omitted on the assumption that these would be done by individual growers rather than professional applicators. There were as many as 28 sequential days with pesticide applications (rounded to 1 month), and an average of 37 days per year (rounded to 1 month). Based on these data, seasonal and annual exposure to methidathion by workers involved in airblast applications is estimated occur over 1 month.

For M/L of WP products in support of airblast applications, SADD is estimated to be 0.053 mg/kg/day for two months, AADD is estimated at 0.004 mg/kg/day, and LADD is estimated at 0.002 mg/kg/day (Table 9). Exposure estimates for airblast applicators are 1.46 mg/kg/day for one month (SADD), 0.122 mg/kg/day (AADD), and 0.065 mg/kg/day (LADD).

#### Ground Applications, Groundboom.

Significant exposure scenarios involving groundboom applications are M/L and applicator. Groundboom M/L/A were assumed to have exposures in the range of M/L and applicators (exposure estimates are normalized to an 8-hour day, and M/L/A would mix/load part of the day, and apply for the remainder). All M/L exposure estimates (in support of aerial, airblast, and groundboom applications) used the same surrogate PHED data, with the same clothing and PPE

assumptions; the same protection factors were applied to the PHED results. These assumptions and protection factors were discussed above in the aerial applications section. Applicators were assumed to use clothing and PPE listed on product labels, for reasons stated in the California Requirements section. The groundboom applicator scenario included use of either truck or tractor, and an open cab was assumed.

Two protection factors were applied to PHED results for applicators (Appendix 6): a 90% protection factor was applied to hand exposure for use of gloves (Aprea *et al.*, 1994), and a 90% protection factor was applied to inhalation exposure for use of a respirator (NIOSH, 1987). The protection factor for gloves was needed because the applicator PHED subset with gloves gave results with insufficient numbers of high-quality observations, and the subset used did not include gloves (data were from studies conducted outside of California between 1979 and 1992, prior to implementation of field safety requirements in the federal Worker Protection Standard in 1995; study data should not be considered as evidence suggesting that handlers currently applying methidathion via groundboom would not wear gloves).

The acute exposure estimate for M/L was 0.158 mg/kg/day (Table 9). For the applicator scenario, the acute exposure estimate was 0.177 mg/kg/day. U.S. EPA estimated ADD for M/L and groundboom applicators wearing long-sleeved shirts, long pants, shoes and socks, and using respirators, at 0.011 and 0.016 mg/kg/day, respectively (Travaglini, 1999).

Groundboom applications are common in row and field crops, such as alfalfa, artichokes, cotton, and safflowers. For the purpose of estimating handler exposure all ground applications to these crops were assumed to be groundboom applications. PUR data from Monterey County, where most ground applications to these crops occur, were examined from the five-year period, 2000 – 2004 (DPR, 2006b). Days in which fewer than 40 acres were treated (i.e., amounts taking less than 4 hours to treat) were not included, based on the assumption that individual growers rather than professional applicators would treat these amounts. There were as many as 60 sequential days with pesticide applications (rounded to two months), and an average of 64 days per year (rounded to two months). Based on these data, seasonal use of methidathion by workers involved in groundboom applications is estimated to be two months, and annual exposure is estimated to occur over total of two months.

For M/L of WP products in support of groundboom applications, SADD is estimated to be 0.063 mg/kg/day for three months, AADD is estimated at 0.011 mg/kg/day, and LADD is estimated at 0.006 mg/kg/day (Table 9). Exposure estimates for groundboom applicators are 0.044 mg/kg/day for three months (SADD), 0.007 mg/kg/day (AADD), and 0.004 mg/kg/day (LADD).

# Applications with Backpack Sprayer

The significant exposure scenario for applications with a backpack sprayer is M/L/A. Workers in this M/L/A scenario were assumed to use clothing and PPE listed on product labels. A 90% protection factor was applied to inhalation exposure data for use of a respirator (NIOSH, 1987). The estimated acute ADD for M/L/A using backpack sprayers was 0.191 mg/kg/day (Table 9). U.S. EPA estimated a lower ADD, 0.007 mg/kg/day (Travaglini, 1999).

Backpack sprayers are versatile application tools that can be used in small acreages, spot spraying in locations that are difficult to reach with larger equipment, or in cases where larger equipment is unavailable (Landgren, 1996). In its exposure scenario, U.S. EPA assumed use primarily in applications to nursery stock, with a daily application of 40 gallons (Travaglini, 1999; U.S. EPA, 2002); these assumptions were also used by DPR as no better information was available.

For the purpose of estimating long-term handler exposure all ground applications to nursery stock were assumed to be backpack sprayer applications. PUR data from the five-year period, 2000 to 2004, from the four counties with the most use (Fresno, Kern, Stanislaus and Tulare) were examined (DPR, 2006b). Three of these counties (Fresno, Kern, and Tulare) are adjacent to one another, and were considered together; Stanislaus County was considered separately. Numbers of sequential days with pesticide applications (and not more than two consecutive days in the interval without applications) were totaled for an estimate of seasonal exposure duration, and numbers of days per year were totaled for annual exposure estimates. In all counties, days totaled much less than one month. There were never more than four sequential days with pesticide applications in any year. In Fresno, Kern, and Tulare counties, applications occurred an average of six days per year. In Stanislaus County, methidathion applications averaged just four days per year. Based on these data, seasonal and annual exposures are not anticipated to occur for handlers involved in methidathion applications using backpack sprayers.

# **Applications with Low-Pressure Handward**

The significant exposure scenario for applications with a low-pressure handwand is M/L/A. Workers in this M/L/A scenario were assumed to use clothing and PPE listed on product labels. A 90% protection factor was applied to inhalation exposure data for use of a respirator (NIOSH, 1987). The estimated acute ADD for M/L/A using low-pressure handwands was 0.0034 mg/kg/day (Table 9). U.S. EPA estimated a lower ADD, 0.00031 mg/kg/day (Travaglini, 1999).

The significant exposure scenario for low-pressure handwand M/L/A was assumed to be in nursery stock, which is in agreement with the U.S. EPA assumption (Travaglini, 1999; U.S. EPA, 2002). As with backpack sprayers, for the purpose of estimating exposure to handlers using low-pressure handwands all ground applications to nursery stock were assumed to have been made with low-pressure handwands. Obviously, the same applications could not all have been made with both methods; however, in the absence of other information no better assumption can be made. As with handlers using backpack sprayers, seasonal and annual exposures are not anticipated to occur.

#### **Fieldworkers**

Significant exposure scenarios for reentry workers are assessed below. For each of these scenarios, exposures of workers reentering fields treated with methidathion were estimated from methidathion DFR on the same or surrogate crops. Transfer factor (TF) estimates were based on the crop and the activity of the worker. The absorbed daily dosage (ADD) was calculated as shown in Equation 3 (Zweig *et al.*, 1980; Zweig *et al.*, 1985), using a dermal absorption (DA) of 50% (Donahue, 1996), a default exposure duration (ED) of 8 hours, and a default body weight

(BW) of 70 kg, based on the mean body weight of the adult U.S. population (U.S. EPA, 1997). Acute exposure estimates for fieldworkers are summarized in Table 10. Seasonal, annual, and lifetime exposure estimates are summarized in Table 11.

Equation 3. Calculation of Absorbed Daily Dosage from Plant Surface Residues <sup>a</sup>

$$ADD (\mu g / kg / day) = \frac{DA \times DFR (\mu g / cm^{2}) \times TF (cm^{2} / hr.) \times ED (hrs. / day)}{BW(kg)}$$

Table 10. Acute Exposures to Methidathion Estimated for Reentry Workers

Exposure scenario	DFR (μg/cm <sup>2</sup> ) <sup>a</sup>	TF (cm <sup>2</sup> /hr) <sup>b</sup>	Acute ADD (mg/kg/day) <sup>c</sup>
Scouting in Cotton/Safflower <sup>d</sup>	0.815	2,000	0.093
Harvesting/Thinning Citrus <sup>e</sup>	0.041	3,000	0.007
Thinning of Artichokes <sup>f</sup>	0.815	300	0.014

<sup>&</sup>lt;sup>a</sup> Dislodgeable foliar residue (DFR) estimated for appropriate restricted entry interval (REI).

- Exposure duration = 8 hr
- Dermal Absorption = 50% (Donahue, 1996)
- Body weight = 70 kg, based on mean for adult U.S. population (U.S. EPA, 1997)
- <sup>d</sup> REI = 48 hours. DFR derived from Rosenheck (1998b). TF from Dong (1990).
- <sup>e</sup> REI = 30 days. DFR derived from Rosenheck (1998a). TF from U.S. EPA (2000).

Reentry workers are not required to wear PPE unless entering before expiration of the REI. As much reentry work occurs in hot weather and for several hours each day, PPE is often not worn by fieldworkers. Therefore, fieldworker exposure calculations were not corrected with any protection factor. Acute exposures were estimated at the expiration of the REI for all activities (Table 10). For long-term exposure estimates it was assumed that workers would not always enter fields at the expiration of the REI. DPR does not assume immediate reentry for long-term estimates because over longer periods of time, a worker is expected to encounter a range of daily exposures (i.e., DPR assumes that with increased exposure duration, repeated daily exposure at the upper-bound level is unlikely). Most activities performed by reentry workers (e.g., weeding, thinning, harvesting) are independent of pesticide applications. Even reentry scouting is not necessarily related to application of a particular pesticide, as multiple pests are found in crops, and often multiple pesticides are used. Seasonal, annual and lifetime exposures were estimated at an assumed average reentry of REI + 7 days for cotton scouts and artichoke thinners, and REI + 10 days for workers harvesting or thinning citrus (Table 11). These assumed average reentry days were not based on data; rather, they were based on the reasonable assumption that workers may enter fields an average of 7 - 10 days after expiration of the REI.

Studies of reentry worker exposure in crops treated with methidathion (Hensley, 1981c), as well as with other OPs (Ware et al., 1973, 1974, 1975; Popendorf et al., 1979), suggest that inhalation

<sup>&</sup>lt;sup>a</sup> ADD: Absorbed Daily Dosage. DA: Dermal Absorption. DFR: Dislodgeable Foliar Residue. TF: Transfer Factor. ED: Exposure Duration. BW: Body Weight.

<sup>&</sup>lt;sup>b</sup> Transfer factor (TF) is rate of residue transfer to skin.

<sup>&</sup>lt;sup>c</sup> Acute Absorbed Daily Dosage (Acute ADD) calculated from Equation 3. Assumptions include:

<sup>&</sup>lt;sup>f</sup> REI = 48 hours. DFR (surrogate, cotton) derived from Rosenheck (1998b). TF from U.S. EPA (2000).

is a relatively minor exposure route. U.S. EPA also concluded that inhalation exposure of reentry workers would be negligible (Travaglini, 1999). Only dermal exposure was considered for fieldworkers.

Table 11. Estimates of Reentry Worker Exposure to Methidathion

Exposure scenario	SADD (mg/kg/day) <sup>a</sup>	AADD (mg/kg/day) <sup>b</sup>	LADD (mg/kg/day) <sup>c</sup>
Scouting in Cotton/Safflower <sup>d</sup>	0.0045	0.0011	0.0006
Harvesting/Thinning Citrus <sup>e</sup>	0.0024	0.0008	0.0004
Thinning Artichokes f	0.0007	0.0001	0.00006

<sup>&</sup>lt;sup>a</sup> Seasonal Average Daily Dosage is a mean estimate of absorbed dose, calculated from Equation 3. Dislodgeable foliar residue (DFR) estimates are given below for each scenario. Transfer factors are listed in Table 10.

## **Scouting in Cotton and Safflower**

Cotton and safflower scouts are subject to occupational exposure from contact with dislodgeable methidathion residues that have accumulated on treated foliage. The REI is 48 hours for both crops. In the absence of adequate exposure data for workers entering treated fields, residue decay data and transfer factors were used to estimate worker exposure at expiration of the REI (Table 10). DFR was estimated based on a study done in cotton in California (Rosenheck, 1998b), as discussed above in the Environmental Concentrations section. Transfer factors were derived from a series of studies in which several OPs were applied to cotton (Ware *et al.*, 1973, 1974, 1975). Geometric mean transfer factors were computed for bare hands (950 cm²/hr), the clothed upper body (102 cm²/hr), and the clothed lower body (964 cm²/hr). The potential dermal transfer factor for the whole body of cotton scouts (2,000 cm²/hr) was calculated by summing these individual geometric mean transfer factors (Dong, 1990). The acute ADD for cotton/safflower scouts was estimated to be 0.093 mg/kg/day.

Surrogate data from the PUR were used to estimate intervals for seasonal and annual exposures. As reentry workers can move between fields, it is possible that they may potentially be exposed throughout the year. However, PUR data show that for many crops methidathion use does not occur throughout the year, and that for others there are times when relatively few applications are made. It is reasonable to assume that an individual worker is less likely to be exposed to methidathion during these relatively low-use intervals. Thus, rather than assume that workers are exposed throughout the year, annual use patterns are plotted based on monthly PUR data. In 2004, only 325 applications were made throughout California to artichokes (see Table 3), and 10% of that would average to about an application per day. Annual exposure to methidathion is assumed to be limited to the months when use is relatively high (defined as 10% or more of annual use each month). Seasonal exposure intervals are assumed to be the longest contiguous period during which monthly use is at least 10% of annual total; seasonal use may involve fewer months than annual use.

Annual Average Daily Dosage = ADD x (annual use months per year)/(12 months in a year).

<sup>&</sup>lt;sup>c</sup> Lifetime Average Daily Dosage = AADD x (40 years of work in a lifetime)/(75 years in a lifetime).

<sup>&</sup>lt;sup>d</sup> DFR (Day 9) = 0.040. Estimated seasonal exposure is 3 months; estimated annual exposure is 3 months.

<sup>&</sup>lt;sup>e</sup> DFR (Day 40) = 0.014. Estimated seasonal exposure is 3 months; estimated annual exposure is 4 months.

 $<sup>^{</sup>f}$  DFR (Day 9) = 0.040. Estimated seasonal exposure is 2 months; estimated annual exposure is 2 months.

Figure 2 shows the relative numbers of cotton and safflower acres treated with methidathion, averaged on a monthly basis for the five-year period, 2000-2004 (DPR, 2006b; queried May 19, 2006). Applications made in the entire state (all counties) are plotted in Figure 2, as are applications in the high-use counties of Fresno, Kern, and Kings. These counties are adjacent to one another, and examination of Figure 2 shows that the use pattern in these counties is very similar to the state of California as a whole. In these three counties, most applications occurred in late spring and early summer, with 68% of all applications occurring in June; all applications occurred between May and July. For seasonal and annual exposure estimates, it was assumed that scouts were exposed on each workday for these three months. The SADD was estimated to be 0.0045 mg/kg/day, the AADD was estimated to be 0.0011 mg/kg/day, and the LADD was estimated at 0.0006 mg/kg/day (Table 11).

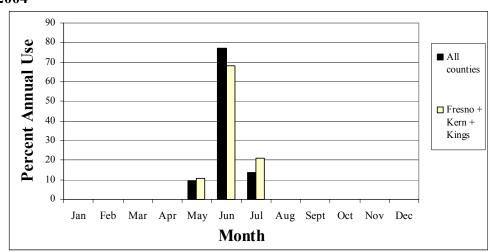


Figure 2. Applications of Methidathion to Cotton and Safflower in Selected Counties, 2000 -2004  $^a$ 

U.S. EPA estimated exposure of cotton and safflower scouts using DFR data from a study done in cotton in North Carolina and Texas (Rosenheck, 1998b). U.S. EPA chose these data because DFR dissipated more slowly at sites in these states than at a site in California, resulting in more conservative exposure estimates (Travaglini, 1999). The differences in DFR between sites were not substantial (e.g., initial post-application DFR values differed by less than 2-fold between sites, and after 14 days the substantially reduced DFR values were still within an order of one another), and might have been simply part of the variation that's normally seen in field studies (Brouwer *et al.*, 1997). Reentry into early-season cotton at Day 2 post-application was estimated by U.S. EPA to result in a dermal dose in the range of 0.14-0.59 mg/kg/day (Travaglini, 1999). With respect to long-term exposures, U.S. EPA stated that such exposures were not reasonable, as scout exposure to foliage treated with methidathion was never likely to exceed 7 days (Travaglini, 1999).

<sup>&</sup>lt;sup>a</sup> Percent calculations based on acres treated (DPR, 2006b; queried May 19, 2006).

# **Harvesting in Citrus**

Under California regulation, the REI following applications to citrus is 30 days (3 CCR 3772). The maximum application rate of methidathion to citrus is 5.0 lbs AI/acre. In the absence of adequate exposure data for workers entering treated fields, residue decay data and transfer factors were used to estimate worker exposure at the expiration of the REI (Table 10). DFR data from a study done in California were used (Rosenheck, 1998a), and a transfer factor of 3,000 was used (Dawson, 2003). The acute ADD was estimated to be 0.007 mg/kg/day.

Figure 3 summarizes numbers of citrus acres treated with methidathion, averaged on a monthly basis for the five-year period, 2000-2004 (DPR, 2006b; queried May 19, 2006). Applications made in the entire state (all counties) are plotted in Figure 3, as are applications in the high-use counties of Fresno, Kern, and Tulare. These three counties are adjacent to one another, and examination of Figure 3 shows that the use pattern in these counties is very similar to the state of California as a whole. Within the high-use counties during the five-year period considered, the majority of the use (80%) occurred in June through August and October; statewide, 78% of the annual use occurred in those four months.

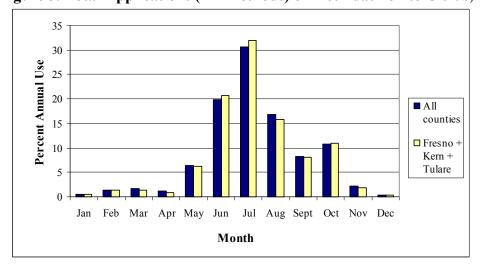


Figure 3. Total Applications (All Methods) of Methidathion to Citrus, 2000 – 2004 a

These data were compared to the task-specific data on cultivation activities in oranges that were available in the California Farm Worker Activity Profile database (CFWAP; Edmiston *et al.*, 1999). Within CFWAP, data were available on citrus (grapefruit, lemon and orange) harvesting in four counties in the San Joaquin Valley; data on oranges from Fresno and Tulare were used. Harvesting of oranges occurs year-round, with peak intervals in January – February and June – August in Fresno County, and peak intervals in January – April and June – September in Tulare County (Edmiston *et al.*, 1999). Because harvesting oranges is done year-round, it suggests that worker exposure to methidathion may occur during the four months (June – August, October) when methidathion is applied most often. Based on these data, seasonal exposure to methidathion by citrus harvesters is estimated to be 0.0024 mg/kg/day for the contiguous 3 months (June – August). The estimated annual exposure (AADD) was 0.0008 mg/kg/day, and the estimated lifetime exposure (LADD) was 0.0004 mg/kg/day (Table 11).

<sup>&</sup>lt;sup>a</sup> Percent calculations based on acres treated (DPR, 2006b; queried May 19, 2006).

# **Thinning of Artichokes**

In artichokes, thinning was the only reentry activity considered to have the potential for significant methidathion exposure. As stated in the Significant Exposure Scenarios section, harvesting of artichokes would not be expected to result in significant exposure to methidathion, as use occurs only in the interval between planting/cut-back and bud formation. In the absence of adequate exposure data for workers entering treated fields, residue decay data and transfer factors were used to estimate worker exposure at the expiration of the REI (Table 10). The default transfer factor of 300 was used to estimate fieldworker exposure (U.S. EPA, 2000). No DFR data were available for methidathion applied to artichokes; a surrogate DFR was used based on data from cotton (Rosenheck, 1998b). The acute ADD was estimated at 0.014 mg/kg/day.

According to the product labels, methidathion may be applied up to eight times per season to artichokes. Applications can begin in newly planted fields, and continue until buds appear. Worker activity data for cultivation activities in artichokes are not available in the CFWAP database (Edmiston *et al.*, 1999). However, publications describing cultivation practices are available (e.g. De Vos, 1992). Artichokes may be cut back any time of the year (De Vos, 1992); thus, workers may reenter fields anytime throughout the year.

Figure 4 summarizes applications of methidathion to artichokes in Monterey County and statewide, based on mean numbers of acres treated each month for the five year period, 2000-2004 (DPR, 2006b; queried May 19, 2006). In Monterey County, an average total of 82% of annual use occurred in the high-use period (defined as > 10% of annual use in each month) during the interval of June and July (Figure 4). Seasonal exposure was estimated to be 0.0007 mg/kg/day for 2 months. Annual exposure duration also was estimated to be 2 months. The AADD estimate was 0.0001 mg/kg/day, and the LADD was estimated at 0.00006 mg/kg/day (Table 11).

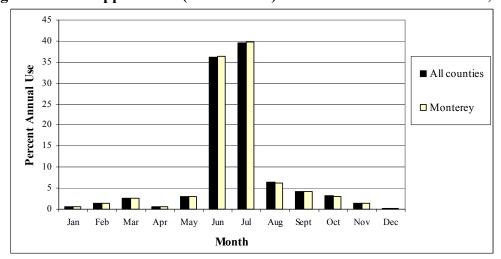


Figure 4. Total Applications (All Methods) of Methidathion to Artichokes, 2000 – 2004 <sup>a</sup>

<sup>&</sup>lt;sup>a</sup> Percent calculations based on acres treated (DPR, 2006b; queried May 19, 2006).

## Mitigation Measures Proposed by U.S.EPA

Several measures were proposed by U.S. EPA (2002) to mitigate occupational and environmental risks of methidathion use. Proposed measures that would affect handler and reentry exposure estimates are summarized in Appendix 9. Revised exposure estimates, reflecting anticipated exposures if these measures were implemented, also are summarized in Appendix 9.

U.S. EPA (2002) proposed to mitigate handler exposures mainly by increasing PPE requirements and engineering controls, and to mitigate reentry exposure by increasing the REI to 3 days for all uses (note that California's REI regulation (3 CCR 6772) requires an extended REI of 30 days in citrus treated with methidathion).

Since release of U.S. EPA (2002), the registrant has been in negotiation with U.S. EPA and has submitted draft labels for approval, which is pending. DPR remains in communication with the registrant to verify status of newer labels.

# **Ambient Air and Bystander Exposures**

Ambient air and application site air monitoring detected methidathion, suggesting that the public may be exposed to airborne methidathion. Individuals might be exposed to methidathion if they are working adjacent to fields that are being treated or have recently been treated (bystander exposure). Also, air monitoring studies in Tulare and Sacramento counties suggest that airborne methidathion exposures are possible in areas that are far from application sites (ambient air exposure). Ambient air and bystander exposures are perhaps more likely in California than in other parts of the U.S. because of the close proximity of urban and agricultural areas in parts of the state where the greatest pesticide use occurs (CAST, 2002). Public exposure to airborne methidathion was estimated, based on monitoring studies of methidathion at application sites and in ambient air. See the Environmental Concentrations section for study details.

#### **Ambient Air**

Methidathion concentrations in ambient air were higher in Tulare County than in Sacramento County (Royce *et al.*, 1993a; Majewski and Baston, 2002). This coincided with greater use in Tulare County than in Sacramento County during the monitoring periods; total annual use of methidathion was 75,582 pounds in 1991 in Tulare County and average annual methidathion use in Sacramento County in 1996 and 1997 was 533 pounds (see Figure 1 and Figure 5).

Whereas ambient air monitoring was done year-round in Sacramento County (Majewski and Baston, 2002), it was only done for four weeks in Tulare County, from June 27 through July 25 (Royce *et al.*, 1993a). Figure 1 shows the use of methidathion in Tulare County in 1991, the year ambient air sampling was done in Tulare County. Figure 1 shows that the highest use of methidathion in Tulare County in 1991 occurred during June, and that little use occurred in March, April, May, November and December.

In contrast to Tulare County, in Sacramento County during air monitoring done in 1996 – 1997 very little methidathion was used, 332 pounds in 1996 and 733 pounds in 1997. In 1996, use occurred in January, June and July; in 1997 nearly all use occurred in January (Figure 5; note scale on y-axis). This use coincided with the two samples collected in January by Majewski and Baston (2002), in which methidathion was detected. Examination of use in 1998 – 2002 (data not shown) suggests that methidathion use in Sacramento County has remained low; in fact, no use was reported in 2000 through 2002. Based on the use data and limited detection of methidathion, data from Sacramento County were not used to estimate ambient air exposure.

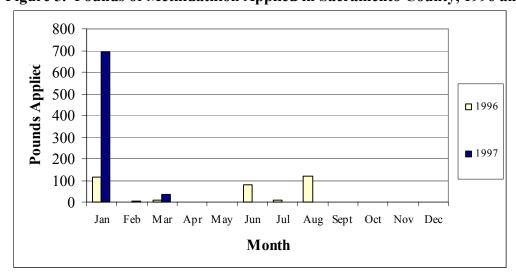


Figure 5. Pounds of Methidathion Applied in Sacramento County, 1996 and 1997 a

Table 12 summarizes ambient air exposure estimates to methidathion and its oxon, based on monitoring done in Tulare County (Royce *et al.*, 1993a). Following DPR practice, acute ADDs were calculated with 95% percentile concentrations estimated using lognormal methods. DPR's experience with many large environmental datasets has shown that they are usually well described by the lognormal distribution.

Acute ADD for ambient air exposure was calculated using the 95<sup>th</sup> percentile estimate, based on air monitoring data from Site J. Acute ADD for methidathion was estimated to be 0.000110 mg/kg/day for infants and 0.000052 mg/kg/day for adults (Table 12). These estimates are slightly lower than exposure estimates recently published by Lee *et al.* (2002). Based on air monitoring data from Royce *et al.* (1993a), Lee *et al.* (2002) used a probabilistic analysis to estimate exposures to adults and children in Tulare County. Acute exposure estimates for children ranged 0.0002 – 0.0004 mg/kg/day (Table 5 in Lee *et al.*, 2002), and for adults, 0.00014 – 0.0002 mg/kg/day (Table 6 in Lee *et al.*, 2002).

Acute ADD for methidathion oxon was estimated to be 0.000047 mg/kg/day for infants and 0.000022 mg/kg/day for adults (Table 12). Lee *et al.* (2002) did not estimate exposures to methidathion oxon.

<sup>&</sup>lt;sup>a</sup> Pounds applied by all methods to all crops in Sacramento County (DPR 2006b; queried May 25, 2006).

Table 12. Ambient Air Exposure Estimates for Persons Exposed to Methidathion and Methidathion Oxon <sup>a</sup>

	Air conce	ntration b	95 <sup>th</sup>	Acute	$ADD^{d}$	Seasona	al ADD <sup>e</sup>	Annua	$IADD^f$
	$(\mu g/1)$	$m^3$ )	percentile	(mg/k	g/day)	(mg/k	g/day)	$(\mu g/k)$	g/day)
Site	Mean	SD	conc. c	Infants	Adults	Infants	Adults	Infants	Adults
Methidath	<u>ion</u>								
Site J g	0.069	0.144	0.186	0.000110	0.000052	0.000041	0.000019	0.000031	0.000014
Methidath	ion Oxon								
Site J <sup>g</sup>	0.032	0.027	0.079	0.000047	0.000022	0.000019	0.000009	0.000014	0.000007
a D-4- C	•, •	1	1 0 4	· 1001 (D	, 1 1	002			

<sup>&</sup>lt;sup>a</sup> Data from monitoring done in Tulare County in 1991 (Royce et al., 1993a).

- Infant inhalation rate = 0.59 m<sup>3</sup>/kg/day (Layton, 1993; US EPA, 1997)
- Adult inhalation rate = 0.28 m<sup>3</sup>/kg/day (Wiley et al., 1991; US EPA, 1997; OEHHA, 2000)
- Inhalation absorption is assumed to be 100%

Ambient air monitoring was done in 1991, during a time when high methidathion use was anticipated in Tulare County (Royce *et al.*, 1993a). Figure 4 confirms that use was high during the ambient air monitoring period: a total of 30,000 lbs was applied in June and 10,000 lbs in July. Nevertheless, the highest use interval was not captured, as monitoring was not begun until the end of June. Examination of daily methidathion use in Tulare County for 1991 (data not shown) reveals that the highest daily use (2,374 lbs) occurred on June 21; during ambient air monitoring daily use varied between 27 lbs and 1,401 lbs. On July 10, the date of the highest recorded ambient air concentration (see Table 4), a total of 399 lbs was used in Tulare County; on the preceding two days, 202 lbs and 612 lbs were used (DPR, 2005b; queried April 27, 2004).

To estimate annual and lifetime ambient air exposures to methidathion and methidathion oxon, temporal patterns were investigated by plotting pounds applied per month for each of the past five years for which data are available. Figure 6 displays monthly use patterns in Tulare County for 2000 - 2004. Comparison of Figure 6 with Figure 1 suggests that the majority of methidathion use in recent years still occurs in two peaks, one in summer and one in winter. In Figure 6, the summer peak from June through August accounts for 46% of annual use, and the winter peak from January through February accounts for an additional 34%; together, these peaks account for 80% of annual methidathion use. Methidathion use between September and December, accounts for about 5% each month (because multiple crops were treated, high use for this scenario is taken at > 5% of the annual total). Thus, the estimated high-use period ( $\geq$  5% of annual use) for seasonal and annual exposure estimates is nine months (May – August and October – February).

<sup>&</sup>lt;sup>b</sup> Arithmetic mean and standard deviation (SD). Calculated using ½ limit of detection (LOD) for samples < LOD.

<sup>&</sup>lt;sup>c</sup> Concentration (in μg/m³) used for acute exposure estimates. Calculated using lognormal distribution methods.

<sup>&</sup>lt;sup>d</sup> Acute Absorbed Daily Dosage (mg/kg/day) = (95<sup>th</sup> percentile upper bound air concentration) x (inhalation rate). Calculation assumptions include:

<sup>&</sup>lt;sup>e</sup> Seasonal ADD = (mean air concentration) x (inhalation rate). Calculation assumptions as above. Estimated season for SADD is 9 months.

f Annual ADD = (Seasonal ADD) x (annual use months per year)/12. Annual use estimated at 9 months.

<sup>&</sup>lt;sup>g</sup> Site J = Jefferson Elementary School in Lindsay. This was the site with most samples above the LOD (see Table 4).

Although Figure 6 shows percent annual use each month, methidathion use in Tulare County has declined since ambient air monitoring has been done in 1991 and 1994. Figure 7 summarizes annual use in Tulare County between 1991 and 2004. Figure 7 shows that annual methidathion use in Tulare County was highest in 1993, and that use has declined since then. For example, use in 2000 - 2004 was less than a quarter of use in either 1991 or 1994.

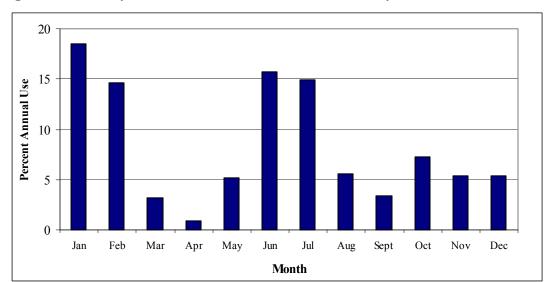


Figure 6. Monthly Use of Methidathion in Tulare County, 2000-2004 a

<sup>&</sup>lt;sup>a</sup> Pounds applied by all methods to all crops in Tulare County (DPR 2006b; queried May 25, 2006).

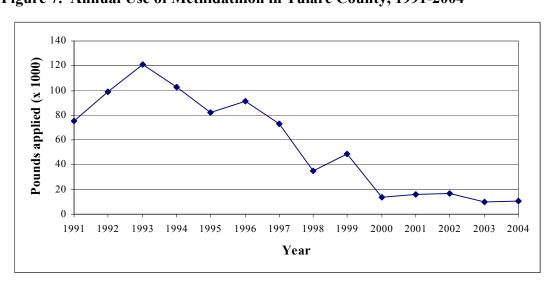


Figure 7. Annual Use of Methidathion in Tulare County, 1991-2004 <sup>a</sup>

Figure 1 shows that in 1991 more than 30,000 lbs of methidathion was applied in June. During the most recent five years for which data are available (2000 - 2004), monthly methidathion use

<sup>&</sup>lt;sup>a</sup> Thousand of pounds applied by all methods to all crops in Tulare County (DPR 2006b; queried May 25, 2006).

was never above 5,000 lbs (data not shown). However, examination of daily use in the PUR reveals that as recently as 2002 daily use in June was as high as 896 lbs; this is greater than daily use seen in mid-July 1991, when the highest methidathion concentrations occurred during ambient air monitoring (the highest daily use in June 2003 was 268 lbs). Depending on how use is distributed throughout the county, ambient air exposure in some parts of Tulare County might be as high as suggested by air monitoring done in 1991, and insufficient data are available to support lower exposure estimates. As previously explained in the Pesticide Application and Use section, methidathion use has been decreasing in California for several reasons, but there is no mechanism to prevent use from increasing again later. For this reason, annual exposure estimates rely on use patterns shown in Figure 6.

Seasonal and annual exposure estimates reported in Table 12 were based on 9 high-use months. Seasonal ADD for methidathion was estimated to be 0.000041 mg/kg/day for infants and 0.000019 mg/kg/day for adults. Annual ADD was estimated to be 0.000031 mg/kg/day for infants and 0.000014 mg/kg/day for adults. Seasonal ADD for methidathion oxon was estimated to be 0.000019 mg/kg/day for infants and 0.000009 mg/kg/day for adults. Annual ADD was estimated to be 0.000014 mg/kg/day for infants and 0.000007 mg/kg/day for adults.

Lee *et al.* (2002) estimated subchronic (> 14 days) and chronic (> 1 year) methidathion exposures for children and adults. For children, subchronic exposure estimates ranged 0.000018 - 0.00018 mg/kg/day and chronic exposure estimates ranged 0.000002 - 0.000012 mg/kg/day. For adults, subchronic exposure estimates ranged 0.00001 - 0.0001 mg/kg/day and chronic exposure estimates ranged 0.000012 - 0.000006 mg/kg/day (Lee *et al.*, 2002). Seasonal exposure estimates in Table 12 are in the range of the probabilistic estimates reported by Lee *et al.* (2002). The annual ADD estimates reported in Table 12 for methidathion are higher, as they are based on assumed constant inhalation rates and ambient air concentrations for 9 months, while the probabilistic estimates reported by Lee *et al.* (2002) assumed a gamma distribution for inhalation rates and a lognormal distribution for air concentrations. Also, Lee *et al.* (2002) reported that only twelve samples of 65 had methidathion concentrations above the limit of quantification (LOQ) of  $0.3 \mu g/m^3$ ; all other samples were assumed to have a methidathion concentration of  $0.003 \mu g/m^3$  (LOQ divided by 100). In spite of these different approaches to the data, however, there was little difference between exposure estimates reported in Table 12 and in Lee *et al.* (2002).

# **Bystanders at Application Sites**

To estimate bystander exposure to methidathion and methidathion oxon in air, data were used from application site monitoring in the 1991 study in Tulare County (Royce *et al.*, 1993a). Table 6 summarizes air concentrations during several monitoring periods at each of these stations. The application monitored by Royce *et al.* (1993a) was less than the maximum allowed, with an application rate of 3.0 lbs AI/acre to 15 acres, for a total application of 45 lbs. Examination of methidathion applied in other airblast applications (DPR, 2006b; data not shown) suggests that this is approximately the 70<sup>th</sup> percentile of applications. The 95<sup>th</sup> percentile application is approximately 180 lbs AI, which is four times as large. Bystanders near a larger orchard or one receiving the maximum application rate would be anticipated to be exposed to higher

concentrations than measured by Royce *et al.* (1993a). The concentrations used to estimate exposure were therefore adjusted (multiplied by 180/45 = 4).

Table 13 summarizes the bystander exposure estimates. The adjusted 24-hour TWA for the north monitoring station was used to estimate exposure to methidathion (4 x 0.75  $\mu g/m^3 = 3.0 \mu g/m^3$ ) and methidathion oxon (4 x 0.22  $\mu g/m^3 = 0.88 \mu g/m^3$ ). Acute ADD for methidathion was 0.00177 mg/kg/day for infants and 0.00087 mg/kg/day for adults. Acute ADD for methidathion oxon was 0.00052 mg/kg/day for infants and 0.00026 mg/kg/day for adults.

Table 13. Bystander Exposure Estimates for Methidathion and Methidathion Oxon <sup>a</sup>

	Adjusted Methidathion Concentration (μg/m³) <sup>b</sup>	Adjusted Methidathion Oxon Concentration (µg/m³) <sup>b</sup>	Inhalation Rate <sup>c</sup>	Absorbed Methidathion Dose <sup>d</sup>	Absorbed Methidathion Oxon Dose <sup>d</sup>
1-Hour A	Absorbed Dose (during hea	avy activity for 1 hour) e			
Infant	12.6	0.76	$0.16 \text{ m}^3/\text{kg/hr}$	0.00315 mg/kg/hr	0.00019 mg/kg/hr
Adult	12.6	0.76	$0.022 \\ m^3/kg/hr$	0.00057 mg/kg/hr	0.000034 mg/kg/hr
Acute A	bsorbed Daily Dosage (Ac	ute ADD) $f$			
Infant	3.0	0.88	0.59 m <sup>3</sup> /kg/day	0.00177 mg/kg/day	0.00052 mg/kg/day
Adult	3.0	0.88	0.28 m <sup>3</sup> /kg/day	0.00087 mg/kg/day	0.00026 mg/kg/day

<sup>&</sup>lt;sup>a</sup> Based on air monitoring done 25 m from a Tulare County orange grove in 1991 (Royce et al., 1993a).

As available information suggests that exposures of less than 24 hours can result in toxicity, 1-hour exposure estimates were calculated based on the highest measured concentration. Maximum concentrations reported by Royce *et al.* (1993a) were adjusted for methidathion (4 x  $3.16 \text{ µg/m}^3 = 12.6 \text{ µg/m}^3$ ) and methidathion oxon (4 x  $0.18 \text{ µg/m}^3 = 0.76 \text{ µg/m}^3$ ). The 1-hour

b Concentrations adjusted from the North station, the application air monitoring site with the highest mean methidathion and methidathion oxon concentration in the 24 hours during and post-application (see Table 6). Concentrations were multiplied by 4, the ratio between the amount of methidathion in the 95<sup>th</sup> percentile application (180 lbs), and 45 lbs, the amount in the application monitored by Royce *et al.* (1993a).

<sup>&</sup>lt;sup>c</sup> Different inhalation rates were used for the 1-hour and acute 24-hour absorbed doses. The inhalation rates for 1-hour absorbed dose estimates were calculated from values reported in Andrews and Patterson (2000), assuming heavy activity and dividing by the median body weight for males and females. Hourly inhalation rates for heavy activity are 1.9 m³/hr for infants (Layton, 1993; U.S. EPA, 1997) and 3.2 m³/hr for adults (Wiley *et al.*, 1991; U.S. EPA, 1997; OEHHA, 2000). Daily inhalation rates are default values from Andrews and Patterson (2000).

d 1-hour absorbed doses assume 1-hour exposure during heavy activity, and are based on highest methidathion and methidathion oxon concentrations measured by Royce *et al.* (1993). Absorbed daily doses assume a typical mixture of activity levels throughout the day and are based on the highest 24-hour time-weighted average (TWA) air concentrations from Royce *et al.* (1993).

<sup>&</sup>lt;sup>e</sup> 1-hour absorbed dose (mg/kg/hr) = (highest 1-hour air concentration) x (inhalation rate). The maximum 1-hour concentrations from Table 6 (3.16  $\mu$ g/m<sup>3</sup> and 0.18  $\mu$ g/m<sup>3</sup>), from the North air monitoring station, were adjusted as described in Footnote <sup>b</sup>.

<sup>&</sup>lt;sup>f</sup> Acute ADD (mg/kg/day) = (TWA air concentration) x (inhalation rate). The 24-hour TWA concentrations from Table 6 (0.75 μg/m<sup>3</sup> and 0.22 μg/m<sup>3</sup>), from the North air monitoring station, were adjusted as described in Footnote  $^b$ .

absorbed dose of methidathion was 0.00315 mg/kg/hr for infants and 0.00057 mg/kg/hr for adults. The 1-hour absorbed dose of methidathion oxon was 0.00019 mg/kg/hr for infants and 0.000034 mg/kg/hr for adults.

Seasonal or annual exposure to application site airborne methidathion or methidathion oxon levels is not expected because repeated nearby applications are not likely, and airborne concentrations are anticipated to reach ambient levels within a few days after the application. Seasonal and ambient air methidathion exposure estimates are given in Table 12.

### **EXPOSURE APPRAISAL**

#### Handlers

### **Use of Surrogate Data**

Exposure estimates for handlers were based on surrogate data, due to lack of acceptable, chemical-specific data. Exposure monitoring data from PHED were used to estimate handler exposures for the various application methods. PHED incorporates exposure data from many studies, each with a different minimum detection level for the analytical method used to detect residues in the sampling media. Moreover, as the detection of dermal exposure to the body regions was not standardized, some studies observed exposure to only selected body parts. Consequently, the subsets derived from the database for dermal exposure may have different numbers of observations for each body part, a fact which complicates interpretation of values taken from PHED. However, use of PHED data provided the best exposure estimates possible. U.S. EPA also relied exclusively on PHED data for handler exposure estimates (Travaglini, 1999; U.S. EPA, 2002).

Upper confidence limits are used for seasonal and chronic estimates based on PHED. For these exposures, UCLs are used not because DPR believes that exposures are consistently greater than the population mean, but because available data are so sparse that it is likely that the sample mean is not close to the true population mean. In exposure monitoring, ranges of sample results can be quite broad, and can include values that are substantially higher than sample means (Grover *et al.*, 1986; Vercruysse *et al.*, 1999). Some studies have reported sample ranges that span as much as three orders of magnitude (e.g., Hines *et al.*, 2001). Thus, it is apparent that handlers could have exposures well above sample means; such estimates are not unreasonable. PHED data in particular pose difficulties because they are poorly characterized for the user, confounding assessment of the match between any given subset and the exposure scenario it is intended to represent. UCLs are used by DPR to address concerns specific to PHED (Powell, 2002).

Data quality grades in PHED have been assigned based on Quality Assurance/Quality Control data provided in exposure study reports. Grades A and B are high-quality grades, with lab recoveries of 90-110% and 80-100%, respectively (field recoveries range 70-120% and 50-120%); grade C represents moderate quality, with lab and field recoveries of 70-120% and 30-120%, respectively; E is the lowest quality grade, and is assigned to PHED data that do not meet

basic quality assurance (U.S. EPA, 1998b). Data quality grades for each PHED data set used in exposure estimates are summarized in the first table of each appendix.

Dermal data quality was generally high in the data sets used to generate exposure estimates, with the exception of those used to estimate exposure to M/L/A using backpack sprayers or low-pressure handwands, in which data quality was moderate. Inhalation data quality was high or moderate, with the exception of the data set used to estimate aerial applicator exposure, in which six of the 16 observations were of low data quality.

The appendices also summarize numbers of observations contained in each PHED subset. Subsets for M/L/A using low-pressure hand wand or backpack sprayer had 9-11 observations for each body part. This is a very small number of observations, increasing the uncertainty in estimates generated from these subsets. Other subsets that are rather small include M/L handling WP in WSP (6-15 observations) and aerial applicator (9-17 observations).

## **DPR and U.S. EPA Estimates**

Handler exposure estimates described in this EAD were generally higher than estimates from U.S. EPA (Travaglini, 1999). Differences in estimates by U.S. EPA (Travaglini, 1999) and DPR (present document) might be anticipated because U.S. EPA used geometric means to summarize PHED data, whereas DPR used arithmetic means, in accordance with the usual practice of DPR. Also, U.S. EPA estimates were based on means rather than the upper confidence limits used by DPR.

Acute ADD calculated by DPR are upper-bound exposure estimates, whereas U.S. EPA calculated only central tendency exposure estimates. DPR believes upper-bound estimates are appropriate for short-term exposures because high-end exposures are possible, and DPR has an obligation to protect all individuals exposed during and after legal uses of methidathion (not just uses under "average" conditions). For short-term exposure estimates, it is irrelevant whether the upper bound is many times the size of the mean; the upper bound is used because data suggest that such exposures can happen.

DPR estimated internal dosages, and assumed a dermal absorption of 50%. U.S. EPA estimated potential exposures, as their Margins of Exposure (MOEs; values calculated for risk assessment purposes) for handlers relied on a dermal study (Travaglini, 1999). Differences in dermal absorption assumptions tended to partially mitigate the differences occurring in PHED values used by U.S. EPA and DPR.

U.S. EPA exposure estimates covered a range of PPE and engineering combinations, and DPR estimates addressed only the combinations required by California and federal regulations. With respect to aerial applicators, U.S. EPA assumes use of closed cockpits in all aerial exposure estimates. In cases where planes with open cockpits can be used, U.S. EPA policy is to require an additional 10-fold safety factor in the risk calculation (U.S. EPA, 1998c). However, the most recent information available about equipment used by aerial applicators shows that open cockpits are relatively rare, but may still be used (NAAA, 2004). As current methidathion product labels do not require closed cockpits, estimates in this EAD assumed open cockpit, which results in

substantially higher estimates. For example, the aerial applicator acute ADD reported in Table 9 is 4.65 mg/kg/day. If a closed cockpit were assumed (but if pilots were not required to wear gloves), the acute ADD would be 0.645 mg/kg/day.

### **Other Defaults**

Handler exposure estimates assumed a default body weight of 70 kg. This value is the mean body weight of the adult U.S. population, rounded to one significant figure (U.S. EPA, 1997), as well as being the value median body weight for adults in the U.S. (Thongsinthusak, 1998). The default value might be underestimated, based on trends in body weights in U.S. populations in general, in which mean weights of adults over age 21 increased between the two most recent intervals (Ogden *et al.*, 2004). As exposure estimates are divided by assumed body weight, underestimates in body weight might result in overestimated exposure.

A default dermal absorption value of 50% was used in this EAD, as no acceptable data were available to support a chemical-specific estimate. DPR is not aware of any properly-conducted study that demonstrated dermal absorption greater than 50% in humans, and although DPR continues to review new studies and is open to changing this default if evidence suggests it is appropriate, based on available data DPR considers 50% dermal absorption to be a health-protective default. However, in the absence of data it is possible that exposure estimates are underestimated by this default, perhaps by as much as two-fold.

Conversely, the estimated inhalation absorption default of 100% might overestimate actual absorption. Data are extremely limited on uptake of pesticides via inhalation, and because of this DPR has decided to use a 100% assumption as a health-protective default. However, this assumption has a practically negligible effect on handler exposure estimates, as inhalation contributes < 1% to the total exposure estimate (see Table 8).

PUR data were used to estimate likely numbers of days workers were exposed, based on the distribution of applications in high-use California counties. These high-use periods describe a recent work history of the handler population, and they probably overestimate the workdays for any single individual. They provide the best available data for long-term exposure estimates, however.

PUR data could perhaps be used more extensively in estimating long-term exposure, by providing central tendency estimates of lbs AI/acre and acres treated; DPR is currently considering such a change. In this EAD, for both short-term and long-term exposure estimates, maximum allowed application rates were used, from product labels. The numbers of acres treated per day were based on defaults recommended by U.S. EPA (2001). These estimates are expected to be conservative but realistic; however, insufficient data exist to evaluate their accuracy.

#### **Fieldworkers**

Acceptable monitoring data were lacking for fieldworker exposures, as for handlers. Exposure estimates for fieldworkers were based on chemical-specific, but not necessarily crop-specific,

DFR values. Residues may dissipate at different rates on different crops, due to factors such as leaf topography and physical and chemical properties of leaf surfaces. DFR dissipation can also vary with weather conditions, which is why DPR relies on California-specific data whenever available. For methidathion, DPR relied on DFR data from studies done in California for both citrus (Rosenheck, 1998a) and cotton (Rosenheck, 1998b). For citrus, U.S. EPA also relied on data from California (Rosenheck, 1998a), while for cotton U.S. EPA relied on DFR data from North Carolina and Texas (Rosenheck, 1998b), resulting in slightly higher exposure estimates.

U.S. EPA used a different No-Observed-Adverse-Effect-Level (NOAEL) for calculating risks for reentry than for calculating handler risks. The NOAEL used for reentry worker risk was from an oral study, meaning that U.S. EPA applied a dermal absorption factor to fieldworker exposure estimates. DPR used a default dermal absorption of 50%, while U.S. EPA (2002) estimated the dermal absorption to be 30%, based on a comparison of oral and dermal toxicity in two studies using rabbits. As explained previously in the Pharmacokinetics section, DPR does not rely on toxicity ratios. Because of the difference in dermal absorption assumptions, reentry exposure estimates calculated by DPR are somewhat greater than those calculated by U.S. EPA.

Extent of contact with foliage, unlike DFR, is not chemical specific, and transfer factor values for various crop activities are readily available, based on studies using other chemicals. Where crop-specific transfer factors were not available, general defaults were used. These defaults were likely to be conservative (U.S. EPA, 2000). However, information is lacking about exposures resulting from some activities, such as weeding and roguing (removal of diseased crop plants) in cotton, and how these exposures might compare with those of scouts.

As with handlers, seasonal exposure estimates for fieldworkers were partly based on PUR data, in that months in which pesticide use overlapped fieldworker activities were considered to be months in which fieldworkers were potentially exposed to pesticides. This is a conservative estimate, which may result in an overestimate of seasonal, annual and lifetime exposures.

## **Ambient Air and Bystander Exposure Estimates**

Public exposures to airborne methidathion and methidathion oxon were estimated based on their concentrations in air and assumptions about their uptake from the air. Inhalation exposure might be overestimated by the default absorption of 100% assumed in exposure calculations. No biomonitoring or other exposure monitoring data were available; in the absence of data, no prediction is possible about the extent to which exposure might be overestimated.

Exposure estimates were provided for adults for consistency with other scenarios, and for infants as likely worst-case estimates because infants have the greatest inhalation rate per body weight. Inhalation rate defaults are based on the best available data, but uncertainties are associated with these defaults and exposures might be underestimated or overestimated to an unknown extent as a result. Infant inhalation rates are based on estimated energy expenditures based on dietary studies of food energy intake (Andrews and Patterson, 2000). Survey data have uncertainties due to recall bias; in fact, as food consumption survey subjects have been shown to consistently underestimate the amount of food they have eaten, national food consumption survey results

used to calculate inhalation rates were adjusted upward to account for an assumed bias (Layton, 1993). Default inhalation rates for adults were based on the activity pattern from survey data, inhalation rate per activity, and default body weights (Andrews and Patterson, 2000). Bystander estimates assumed a mean body weight of 71.8 kg (U.S. EPA, 1997), for consistency with the mean inhalation rates that are used in the calculation (Andrews and Patterson, 2000). This default value might be underestimated, based on trends in body weights in U.S. populations in general, in which mean weights of adults over age 21 increased between the two most recent intervals (Ogden *et al.*, 2004). As exposure estimates are divided by assumed body weight, underestimates in body weight might result in overestimated exposure.

Ambient air exposure estimates were based on one site in Tulare County, and there is insufficient information available to determine how representative this site is. At this site, as at other monitored sites, there were a number of samples in which methidathion, methidathion oxon, or both were not detected. Although ambient air monitoring sites were selected based on anticipated nearby methidathion use, applications of methidathion were not confirmed. It is possible that no applications occurred near the sites where methidathion was not detected, or that the analytical method was not sufficiently sensitive to detect ambient methidathion concentrations. Additionally, each site was monitored only 4 days per week for a relatively short (4-week) period. Fridays through Sundays were not monitored. It is unknown whether days of the week differ systematically in use or ambient air concentrations of methidathion. However, ambient air monitoring occurred during a relatively high-use time (though the highest use was apparently not captured). Use during much of the year is lower than it was in June and July of 1991, particularly in recent years. This suggests that seasonal and annual ambient air exposure estimates based on monitoring done in 1991 are more likely to have been overestimated than underestimated.

For bystander exposure estimates, data from the north monitoring station, 25 m from the application site, were used as a reasonable worst-case estimate for methidathion concentration in air for acute exposure estimates. As the application monitored was smaller than the maximum anticipated application, based on PUR data, airborne concentrations were adjusted upward in an attempt to estimate what a bystander near a larger application might be exposed to. extrapolation required the following assumptions: 1) that concentrations of methidathion and methidathion oxon are proportional to the product of application rate and field size; 2) that weather conditions, which affect offsite air concentrations, are approximately the same for all applications as for the application monitored; and 3) that the application method and equipment is the same for all applications as for the application monitored. If these assumptions are untrue, then exposure might be either over- or underestimated. The first assumption is a combination of two assumptions: first, DPR assumes that pesticide concentrations adjacent to an application site are linearly related to application rate; also, modeling done by DPR's Environmental Modeling Program suggests that concentrations increase with increasing field size (for a field that is square) by a function that's approximately the square root of 2. Because the wind was not in the direction of a sampling station during the application and for several hours afterward, it is possible that the peak concentrations were not captured; thus, exposure could have been underestimated.

Although the quality assurance of the air monitoring was generally acceptable, there were some difficulties. First, there was a positive bias in analyses of both methidathion and methidathion oxon, as shown by spike recoveries that were mostly > 100% and by the detection of methidathion oxon in blanks (interestingly, the reported mean blank of 0.13 µg/sample was less than the LOD for methidathion oxon, which was 0.25 µg/sample; the reason for this is not apparent). Because of the positive bias, samples were not adjusted for spike recoveries, which might result in exposures being overestimated. Also, error might result from the high detection limits for methidathion and methidathion oxon, as concentrations used in ambient air exposure estimates were based largely on samples that were below the LOQ (0.30 µg/sample and 0.75 ug/sample, respectively). For samples above the LOD, reported values were used rather than using ½ LOQ. This was done to prevent exposures from being grossly overestimated, and DPR believes this is the appropriate approach for these data although it could result in exposures being underestimated. Comparison of methidathion concentrations between ambient air monitoring done in 1991 (Table 4) and 1994 (Table 5), at the one site monitored both years, suggests that this is a reasonable approach, considering that methidathion concentrations have greater contributions than methidathion oxon to exposure estimates. Studies conducted near high-use areas and with more appropriate detection limits would give better exposure estimates.

In calculating mean and upper-bound statistics for air monitoring data, ½ LOD was substituted for samples in which methidathion or methidathion oxon was not detected. This was done in accordance with DPR policy, in which ½ the reporting limit (LOD or LOQ) is substituted for any sample below the reporting limit. This was not necessarily the most conservative approach that could be taken toward non-detects. For example, the LOD could have been substituted instead, to give a worst-case concentration estimate (Helsel, 2005). As methidathion was detected in most samples used to estimate exposure, for methidathion concentrations the differences between using LOD and ½ LOD were slight: the mean ambient air methidathion concentration at Site J would be essentially unchanged, and the 95<sup>th</sup> percentile would actually decrease (0.172 µg/m<sup>3</sup> with LOD substituted for non-detects, vs. 0.186 µg/m<sup>3</sup> with ½ LOD). For methidathion oxon, which had numerous non-detects, the approach to non-detects has a greater effect on concentration and exposure estimates. The mean ambient air methidathion oxon concentration at Site J would increase (0.042 μg/m<sup>3</sup> with LOD substituted for non-detects, vs. 0.032 μg/m<sup>3</sup> with ½ LOD), although again the 95<sup>th</sup> percentile would decrease (0.074 µg/m<sup>3</sup> with LOD substituted for non-detects, vs. 0.079 μg/m<sup>3</sup> with ½ LOD). Bystander exposure to methidathion would not be affected, as those estimates are not based on non-detects; however the acute ADD for bystanders exposed to methidathion oxon would increase, as the 24-hour TWA is partially based on non-detects (0.39 μg/m<sup>3</sup> with LOD substituted for non-detects, vs. 0.22 μg/m<sup>3</sup> with ½ LOD).

The  $95^{th}$  percentile ambient air methidathion concentration used to estimate short-term exposures  $(0.186~\mu\text{g/m}^3)$  might result in underestimates. The possibility is suggested by the fact that the  $95^{th}$  percentile is less than concentrations recorded on consecutive days at Site J  $(0.56~\mu\text{g/m}^3)$  and  $0.30~\mu\text{g/m}^3)$ . Nevertheless, DPR considers the  $95^{th}$  percentile concentration to be the appropriate value to use in estimating acute exposures. The fact that the methidathion concentrations were considerably higher on these two consecutive days at this site than on any other day, or at any other site, suggests that these concentrations might have been influenced by nearby applications; i.e., that these elevated concentrations were outliers and not representative of ambient air exposure.

Seasonal or annual exposure to application site airborne methidathion levels is not expected because airborne concentrations are anticipated to reach ambient levels within a few days after the application. Applications of methidathion to citrus are allowed a maximum of twice per year, during the growing season, and deciduous fruit and nut trees receive a maximum of one application per year during the dormant season. Even individuals living near one or more orchards and working near others are unlikely to experience exposures above ambient for more than a few days. As shown in the monitoring data reported by Royce *et al.* (1993), methidathion concentrations in air decrease soon after application. Airborne concentrations of active ingredients also decrease as distance from the application site decreases (MacCollom *et al.*, 1968; Siebers *et al.*, 2003), and it is unlikely that a person would be repeatedly exposed to elevated airborne concentrations in close succession that would result in a seasonal exposure. Acute ADD address exposures from less than one day up to 7 days. DPR believes that intermediate- and long-term exposures to methidathion occur only at ambient concentrations.

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#### **APPENDICES**

Appendix 1: Subset from PHED for Exposure of Mixer/Loaders of Wettable
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Appendix 2: Subset from PHED for Exposure of Mixer/Loaders of Emulsifiable Concentrates.

Appendix 3: Subset from PHED for Exposure of Aerial Applicator.

Appendix 4: Subset from PHED for Exposure of Flagger.

Appendix 5: Subset from PHED for Exposure of Airblast Applicator.

Appendix 6: Subset from PHED for Exposure of Ground Boom Applicator.

Appendix 7: Subset from PHED for Exposure of Mixer/Loader/Applicator Using Backpack Sprayer.

Appendix 8: Subset from PHED for Exposure of Mixer/Loader/Applicator Using Low-Pressure

Handwand.

#### **Notes**

Appendices 1-8 provide detailed information on values used in handler exposure estimates. As described in the Exposure Assessment section, the Pesticide Handlers Exposure Database (PHED) combines exposure data from multiple field monitoring studies of different AIs. The user selects a subset of the data having the same or a similar application method and formulation type as the target scenario. Sufficient information is given in the appendix for each scenario to allow other PHED users to duplicate the subsets and generate the same values.

Once the PHED subsets were generated, inputs for exposure calculations were entered, according to DPR policy. Exposures were requested in mg per pound of AI handled, because the total work time spent within each handling task is not as well defined. For dermal exposure, both actual and estimated head patches were included. For inhalation exposure, the DPR default inhalation rate for handlers of 16.7 L/min was used. Clothing and gloves were chosen based on requirements listed on the label.

Due to an error in PHED (U.S. EPA, 1998b), values for exposure to feet are incorrectly reported, and often omitted entirely. When no exposure was reported for feet, dermal totals were corrected by addition of the best estimate of feet exposure, calculated by multiplying the value for lower legs by 0.52 (ratio of feet/lower leg surface area; U.S. EPA, 1997). In Appendix 3, a value was reported for feet exposure by PHED; this value was replaced by the estimate based on exposure reported for lower legs.

### Appendix 1: M/L, Water Soluble Bags Containing Wettable Powder

**Table 1-1. Description of PHED subsets** <sup>a</sup>

	Specifications used to generate	Actual characteristics of resulting
Parameter	subsets	subsets
Data Quality Grades b	A,B	A,B
Solid Type	Wettable Powder	Wettable Powder
Package Type	Water Soluble Bag	Water Soluble Bag

<sup>&</sup>lt;sup>a</sup> Subsets of Mixer/Loader data in the Pesticide Handlers Exposure Database (PHED). Parameter descriptions are from screens displayed in the PHED program.

Figure 1-1. Summary of results from the Pesticide Handlers Exposure Database (PHED) dermal subset, copied from the results screen displayed after inputs for exposure calculations have been entered a

SUMMARY STATISTICS FOR CALCULATED DERMAL EXPOSURES SCENARIO: Long pants, long sleeves, gloves

PATCH	MI CROGRAMS		IIXED	
LOCATION	Mean	Coef of Var	Geo. Mean	Obs.
HEAD (ALL)	3.51	165.0541	1.1942	15
NECK.FRONT	.423	155.9811	.1734	15
NECK.BACK	.2933	167.61	.0978	15
UPPER ARMS	2.619	17.2127	2.5837	6
CHEST	1.8046	83.2317	1.1207	12
BACK	1.8046	83.2317	1.1207	12
FOREARMS	1.089	17.2176	1.0743	6
THIGHS	4.9023	204.1674	1.6636	12
LOWER LEGS	1.19	86.1261	.7092	12

Subset Name: S3DERMAL.MLOD

Table 1-2. PHED data from dermal, hand, and inhalation subsets <sup>a</sup>

<b>Exposure Category</b>	Exposure (µg/lb AI handled) <sup>a</sup>	Replicates in subset <sup>b</sup>	Short-Term Multiplier <sup>c</sup>	Long-Term Multiplier <sup>c</sup>
Dermal (non-hand) <sup>d</sup>	18.3	12	5	2
Hand (with gloves)	0.056	6	9	2
Inhalation	0.277	12	5	2

<sup>&</sup>lt;sup>a</sup> Results from subsets of Mixer/Loader data in the Pesticide Handlers Exposure Database (PHED).

Table 1-3. Values Used in Short-Term and Long-Term Exposure Calculations <sup>a</sup>

	Short-Term			Long-Term
Total Dermal	5(18.3) + 9(0.56) =	91.8 µg/lb AI handled	2(18.	$(.3) + 2(0.56) = 36.6 \mu\text{g/lb AI handled}$
Inhalation b	5(0.0277) =	0.138 μg/lb AI handled		$2(0.0277) = 0.055 \mu\text{g/lb}$ AI handled

<sup>&</sup>lt;sup>a</sup> Values from Table 1-2. Results rounded to three significant figures.

<sup>&</sup>lt;sup>b</sup> Data quality for Dermal Uncovered, Dermal Covered and Hand are all Grade A or B; Airborne data are all Grade A. Data quality grades are defined in the text and in Versar (1992).

<sup>&</sup>lt;sup>a</sup> Subset criteria included actual and estimated head patches. Of the 15 head observations, all were actual.

<sup>&</sup>lt;sup>b</sup> Median number of replicates was used for Dermal (non-hand).

<sup>&</sup>lt;sup>c</sup> Multipliers are explained in the Exposure Assessment section and in Powell (2002).

<sup>&</sup>lt;sup>d</sup> Dermal total includes addition of default feet value of 0.52 x (value for lower legs); ratio of feet/lower leg surface area (U.S. EPA, 1997).

<sup>&</sup>lt;sup>b</sup> Inhalation data multiplied by 0.1 for use of respirator (NIOSH, 1987).

### Appendix 2: M/L, Closed System, Liquids

Table 2-1. Description of PHED subsets <sup>a</sup>

Parameter	Specifications used to generate subsets	Actual characteristics of resulting subsets
Data Quality Grades b	A,B	A,B
Liquid Type	Emulsifiable concentrate, aqueous suspension, microencapsulated, solution, or undiluted liquid	All emulsifiable concentrate
Mixing Procedure	Closed, mechanical pump or gravity feed	Closed

<sup>&</sup>lt;sup>a</sup> Subsets of Mixer/Loader data in the Pesticide Handlers Exposure Database (PHED). Parameter descriptions are from screens displayed in the PHED program.

Figure 2-1. Summary of results from the Pesticide Handlers Exposure Database (PHED) dermal subset <sup>a</sup> SUMMARY STATISTICS FOR CALCULATED DERMAL EXPOSURES SCENARIO: Long pants, long sleeves, gloves

PATCH	MICROGRAMS	PER LB AI MIX	(ED		
LOCATION	Mean (	Coef of Var	Geo. Mean	Obs.	
HEAD (ALL)	1.6959	121.3279	.9508	22	Subset Name:
NECK.FRONT	1.5225	278.5222	.2418	22	
NECK.BACK	.456	280.8991	.0729	22	S6DERMAL.MLOD
UPPER ARMS	1.3441	96.6967	.7988	21	
CHEST	1.8416	93.4405	1.0577	16	
BACK	1.8416	93.4405	1.0577	16	
FOREARMS	.5474	98.5203	.3206	21	
THIGHS	2.3398	81.9301	1.5773	16	
LOWER LEGS	1.292	85.7276	.8778	21	

<sup>&</sup>lt;sup>a</sup> Subset criteria included actual and estimated head patches. Of the 22 head observations, all were actual.

Table 2-2. PHED data from dermal, hand, and inhalation subsets <sup>a</sup>

<b>Exposure Category</b>	Exposure (µg/lb AI handled) <sup>a</sup>	Replicates in subset <sup>b</sup>	Short-Term Multiplier <sup>c</sup>	Long-Term Multiplier <sup>c</sup>
Dermal (non-hand) d	13.6	21	4	1
Hand (with gloves)	5.72	31	4	1
Inhalation	0.128	27	4	1

<sup>&</sup>lt;sup>a</sup> Results from subsets of Mixer/Loader data in the Pesticide Handlers Exposure Database (PHED).

Table 2-3. Values Used in Short-Term and Long-Term Exposure Calculations <sup>a</sup>

	Shor	rt-Term	Long-Term	
Total Dermal	4(13.55) + 4(5.72) =	77.1 µg/lb AI handled	$1(13.55) + 1(5.71) = 19.3 \mu\text{g/lb AI handled}$	
Inhalation b	4(0.0128) =	0.051 µg/lb AI handled	$1(0.0128) = 0.013 \mu\text{g/lb AI handled}$	

<sup>&</sup>lt;sup>a</sup> Values from Table 2-2. Results rounded to three significant figures.

<sup>&</sup>lt;sup>b</sup> Data quality for Airborne, Dermal Uncovered, Dermal Covered and Hand are all Grade A. Data quality grades are defined in the text and in Versar (1992).

<sup>&</sup>lt;sup>b</sup> Median number of replicates was used for Dermal (non-hand).

<sup>&</sup>lt;sup>c</sup> Multipliers are explained in the Exposure Assessment section and in Powell (2002).

<sup>&</sup>lt;sup>d</sup> Dermal total includes addition of default feet value of 0.52 x (value for lower legs); ratio of feet/lower leg surface area (U.S. EPA, 1997).

<sup>&</sup>lt;sup>b</sup> Inhalation data multiplied by 0.1 for use of respirator (NIOSH, 1987).

# Appendix 3: Aerial Applicator, Liquids, Open Cockpit

Table 3-1. Description of PHED subsets <sup>a</sup>

	Specifications used to generate	Actual characteristics of resulting
Parameter	subsets	subsets
Data Quality Grades b	A,B,C	A,B,C
Liquid Type	Not specified	All emulsifiable concentrate
Solid Type	Exclude granular	none
Application Method	Fixed- or rotary-wing	All fixedwing
Cab Type	Open Cab or Closed Cab with Open	Open Cab; Closed Cab with Open
	Window	Window

<sup>&</sup>lt;sup>a</sup> Subsets of Applicator data in the Pesticide Handlers Exposure Database (PHED). Parameter descriptions are from screens displayed in the PHED program.

Figure 3-1. Summary of results from the Pesticide Handlers Exposure Database (PHED) subset <sup>a</sup> SUMMARY STATISTICS FOR CALCULATED DERMAL EXPOSURES

SCENARIO: Long pants, long sleeves, gloves

PATCH	MICROGRAMS	PER LB AI SP	RAYED		
LOCATION	Mean	Coef of Var	Geo. Mean	Obs.	
HEAD (ALL)	4.212	118.2574	1.2438	10	Subset Name:
NECK.FRONT	.414	143.6715	.1169	10	
NECK.BACK	.3124	139.1485	.0741	10	S17DERMAL.APPL
UPPER ARMS	8.5554	109.6232	5.7532	10	
CHEST	6.3065	158.1987	2.1395	17	
BACK	8.7497	141.5614	3.131	17	
FOREARMS	2.7901	131.7516	1.1744	17	
THIGHS	9.55	157.4126	3.4718	13	
LOWER LEGS	7.4494	138.0769	3.3312	10	

<sup>&</sup>lt;sup>a</sup> Subset criteria included actual and estimated head patches. Of the 10 head observations, 7 were actual and 3 were estimated from nearby patches (Versar, 1992).

Table 3-2. PHED data from dermal, hand, and inhalation subsets <sup>a</sup>

<b>Exposure Category</b>	Exposure (µg/lb AI handled) a	Replicates in subset <sup>b</sup>	Short-Term Multiplier <sup>c</sup>	Long-Term Multiplier <sup>c</sup>
	Ai nanuleu)	subset	Multiplier	Munipher
Dermal (non-hand) <sup>a</sup>	52.2	10	6	2
Hand (with gloves)	9.63	9	6	2
Inhalation	0.573	14	5	2

<sup>&</sup>lt;sup>a</sup> Results from subsets of Mixer/Loader data in the Pesticide Handlers Exposure Database (PHED).

Table 3-3. Values Used in Short-Term and Long-Term Exposure Calculations <sup>a</sup>

	Short-Term	Long-Term
Total Dermal	$6(52.2) + 6(9.63) = 371 \mu\text{g/lb}$ AI handled	$2(52.2) + 2(9.63) = 124 \mu\text{g/lb}$ AI handled
Inhalation b	$5(0.057) = 0.286 \mu\text{g/lb}$ AI handled	$2(0.057) = 0.115 \mu g/lb AI handled$

<sup>&</sup>lt;sup>a</sup> Values from Table 3-2. Results rounded to three significant figures.

<sup>&</sup>lt;sup>b</sup> Data quality for Dermal Uncovered, Dermal Covered, and Hand were Grade A or C; Airborne data were Grade B or C. Data quality grades are defined in the text and in Versar (1992).

<sup>&</sup>lt;sup>b</sup> Median number of replicates was used for Dermal (non-hand).

<sup>&</sup>lt;sup>c</sup> Multipliers are explained in the Exposure Assessment section and in Powell (2002).

<sup>&</sup>lt;sup>d</sup> Dermal total includes addition of default feet value of 0.52 x (value for lower legs); ratio of feet/lower leg surface area (U.S. EPA, 1997).

<sup>&</sup>lt;sup>b</sup> Inhalation data multiplied by 0.1 for use of respirator (NIOSH, 1987).

Subset Name: S7DERMAL.FLAG

## **Appendix 4: Flagger, Liquids**

Table 4-1. Description of PHED subsets <sup>a</sup>

Parameter	Specifications used to generate subsets	Actual characteristics of resulting subsets
Data Quality Grades <sup>b</sup>	A,B	A,B
Liquid Type or Solid Type	Not specified	Emulsifiable concentrate or dry
		flowable.
Application Method	Fixed- or rotary-wing	All rotary-wing

<sup>&</sup>lt;sup>a</sup> Subsets of Flagger data in the Pesticide Handlers Exposure Database (PHED). Parameter descriptions are from screens displayed in the PHED program.

Figure 4-1. Summary of results from the Pesticide Handlers Exposure Database (PHED) subset <sup>a</sup> SUMMARY STATISTICS FOR CALCULATED DERMAL EXPOSURES SCENARIO: Long pants, long sleeves, gloves

PATCH	MICROGRAMS	PER LB AI SE	RAYED	
LOCATION	Mean	Coef of Var	Geo. Mean	Obs.
HEAD (ALL)	11.3028	127.5702	5.6188	18
NECK.FRONT	.9533	134.3334	.5146	18
NECK.BACK	1.4111	215.8529	.4931	18
UPPER ARMS	3.9285	195.1025	.8284	28
CHEST	5.1065	188.8378	1.0384	26
BACK	5.1065	188.8378	1.0384	26
FOREARMS	1.802	179.5283	.3837	28
THIGHS	4.0404	308.6996	.9165	26
LOWER LEGS	2.448	305.6618	.612	28

<sup>&</sup>lt;sup>a</sup> Subset criteria included actual and estimated head patches. Of the 18 head observations, all were actual.

Table 4-2. PHED data from dermal, hand, and inhalation subsets <sup>a</sup>

<b>Exposure Category</b>	Exposure (µg/lb AI handled) "	Replicates in subset <sup>b</sup>	Short-Term Multiplier <sup>c</sup>	Long-Term Multiplier <sup>c</sup>
Dermal (non-hand) <sup>d</sup>	37.4	26	4	1
Hand (no gloves)	5.97	30	4	1
Inhalation	0.200	28	4	1

<sup>&</sup>lt;sup>a</sup> Results from subsets of Mixer/Loader data in the Pesticide Handlers Exposure Database (PHED).

Table 4-3. Values Used in Short-Term and Long-Term Exposure Calculations <sup>a</sup>

	Short-Term	Long-Term
Total Dermal <sup>b</sup>	$4(37.4) + 4(0.597) = 152 \mu\text{g/lb}$ AI handled	$1(37.4) + 1(0.597) = 38.0 \mu\text{g/lb}$ AI handled
Inhalation b	$4(0.020) = 0.080 \mu\text{g/lb}$ AI handled	$1(0.020) = 0.020 \mu\text{g/lb}$ AI handled

<sup>&</sup>lt;sup>a</sup> Values from Table 4-2. Results rounded to three significant figures.

<sup>&</sup>lt;sup>b</sup> Data quality for Dermal Uncovered and Dermal Covered are all Grade A; Airborne and Hand data are all Grade A or B. Data quality grades are defined in the text and in Versar (1992).

<sup>&</sup>lt;sup>b</sup> Median number of replicates was used for Dermal (non-hand).

<sup>&</sup>lt;sup>c</sup> Multipliers are explained in the Exposure Assessment section and in Powell (2002).

<sup>&</sup>lt;sup>d</sup> Dermal total includes addition of default feet value of 0.52 x (value for lower legs); ratio of feet/lower leg surface area (U.S. EPA, 1997).

<sup>&</sup>lt;sup>b</sup> Hand data multiplied by 0.1 for gloves (Aprea et al., 1994). Inhalation data multiplied by 0.1 for use of respirator (NIOSH, 1987).

# Appendix 5: Airblast Applicator, Open Cab

Table 5-1. Description of PHED subsets <sup>a</sup>

Parameter	Specifications used to generate subsets	Actual characteristics of resulting subsets
Data Quality Grades b	A,B	A,B
Liquid Type or Solid Type	Not specified	Emulsifiable concentrate, dry flowable or wettable powder
Application Method	Airblast	Airblast
Cab Type	Open Cab or Closed Cab with	Open Cab or Closed Cab with Open
	Open Window	Window

<sup>&</sup>lt;sup>a</sup> Subsets of Applicator data in the Pesticide Handlers Exposure Database (PHED). Parameter descriptions are from screens displayed in the PHED program.

Figure 5-1. Summary of results from the Pesticide Handlers Exposure Database (PHED) subset <sup>a</sup>

SUMMARY STATISTICS FOR CALCULATED DERMAL EXPOSURES SCENARIO: Long pants, long sleeves, gloves

PATCH	MICROGRAMS	PER LB AI SF	RAYED		
LOCATION	Mean	Coef of Var	Geo. Mean	Obs.	
HEAD (ALL)	778.5762	155.5207	176.2608	42	Subset Name:
NECK.FRONT	37.1325	147.948	12.193	38	
NECK.BACK	27.8342	159.3144	8.7825	42	S9DERMAL.APPL
UPPER ARMS	42.3987	265.4846	6.4049	40	
CHEST	21.8289	177.8784	5.4396	49	
BACK	14.7289	174.1332	4.204	49	
FOREARMS	7.4511	148.7525	2.0066	38	
THIGHS	56.8344	189.968	16.9924	32	
LOWER LEGS	17.2699	129.16	7.0944	32	

<sup>&</sup>lt;sup>a</sup> Subset criteria included actual and estimated head patches. Of the 42 head observations, 41 were actual and 1 was estimated from nearby patches (Versar, 1992).

Table 5-2. PHED data from dermal, hand, and inhalation subsets <sup>a</sup>

THOIC 21 TIED W	10010 0 27 1 1122 4000 11 011 401 1101) 11010) 1110 1110						
<b>Exposure Category</b>	Exposure (µg/lb AI	Replicates in	Short-Term	Long-Term			
	handled) <sup>a</sup>	subset <sup>b</sup>	Multiplier <sup>c</sup>	Multiplier <sup>c</sup>			
Dermal (non-hand) <sup>d</sup>	1,010	40	4	1			
Hand (with gloves)	8.52	18	5	1			
Inhalation	5.41	47	4	1			

<sup>&</sup>lt;sup>a</sup> Results from subsets of Mixer/Loader data in the Pesticide Handlers Exposure Database (PHED).

Table 5-3. Values Used in Short-Term and Long-Term Exposure Calculations <sup>a</sup>

	Shor	rt-Term	Long-Term
Total Dermal	4(1,010) + 5(8.52) =	4,090 μg/lb AI handled	$1(1,010) + 1(8.52) = 1,020 \mu\text{g/lb}$ AI handled
Inhalation b	4(0.541) =	2.16 µg/lb AI handled	1(0.541) = 0.541  ug/lb AI handled

<sup>&</sup>lt;sup>a</sup> Values from Table 5-2. Results rounded to three significant figures.

<sup>&</sup>lt;sup>b</sup> Data quality for Airborne, Dermal Uncovered, Dermal Covered and Hand are all Grade A or B. Data quality grades are defined in the text and in Versar (1992).

<sup>&</sup>lt;sup>b</sup> Median number of replicates was used for Dermal (non-hand).

<sup>&</sup>lt;sup>c</sup> Multipliers are explained in the Exposure Assessment section and in Powell (2002).

<sup>&</sup>lt;sup>d</sup> Dermal total includes addition of default feet value of 0.52 x (value for lower legs); ratio of feet/lower leg surface area (U.S. EPA, 1997).

<sup>&</sup>lt;sup>b</sup> Inhalation data multiplied by 0.1 for use of respirator (NIOSH, 1987).

## Appendix 6: Groundboom Applicator, Open Cab

Table 6-1. Description of PHED subsets <sup>a</sup>

	Specifications used to generate	Actual characteristics of resulting subsets
Parameter	subsets	
Data Quality Grades <sup>b</sup>	A,B	A,B,C
Liquid Type or Solid Type	Not specified	Emulsifiable concentrate or wettable powder
Application Method	Groundboom, Truck or Tractor	Groundboom, Tractor (all)
Cab Type	Open Cab or Closed Cab with Open	Open Cab or Closed Cab with Open Window
	Window	

<sup>&</sup>lt;sup>a</sup> Subsets of Applicator data in the Pesticide Handlers Exposure Database (PHED). Parameter descriptions are from screens displayed in the PHED program.

Figure 6-1. Summary of results from the Pesticide Handlers Exposure Database (PHED) subset <sup>a</sup> SUMMARY STATISTICS FOR CALCULATED DERMAL EXPOSURES

SCENARIO: Long pants, long sleeves, no gloves

PATCH	MICROGRAMS	PER LB AI SE	RAYED		
LOCATION	Mean	Coef of Var	Geo. Mean	Obs.	
HEAD (ALL)	2.7891	136.1192	1.0464	33	Subset Name:
NECK.FRONT	1.5763	167.9503	.3296	23	
NECK.BACK	1.0063	173.5765	.2335	29	S11DERMAL.APPL
UPPER ARMS	1.6914	88.749	1.1637	32	
CHEST	1.7581	98.5154	1.1329	42	
BACK	3.0175	233.2361	1.3959	42	
FOREARMS	2.7301	419.1055	.564	32	
THIGHS	3.1255	185.5703	1.1806	33	
LOWER LEGS	2.1148	172.3425	.7466	35	

<sup>&</sup>lt;sup>a</sup> Subset criteria included actual and estimated head patches. Of the 33 head observations, all were actual.

Table 6-2. PHED data from dermal, hand, and inhalation subsets <sup>a</sup>

<b>Exposure Category</b>	Exposure (µg/lb AI handled) <sup>a</sup>	Replicates in subset <sup>b</sup>	Short-Term Multiplier <sup>c</sup>	Long-Term Multiplier <sup>c</sup>
Dermal (non-hand) d	20.9	33	4	1
Hand (no gloves)	45.6	29	4	1
Inhalation	1.18	22	4	1

<sup>&</sup>lt;sup>a</sup> Results from subsets of Mixer/Loader data in the Pesticide Handlers Exposure Database (PHED).

Table 6-3. Values Used in Short-Term and Long-Term Exposure Calculations <sup>a</sup>

	Short-Term	Long-Term
Total Dermal b	$4(20.9 + 4.56) = 102 \mu\text{g/lb AI handled}$	$1(20.9 + 4.56) = 25.5 \mu\text{g/lb AI handled}$
Inhalation b	$4(0.118) = 0.472 \mu g/lb AI handled$	$1(0.118) = 0.118 \mu\text{g/lb AI handled}$

<sup>&</sup>lt;sup>a</sup> Values from Table 6-2. Results rounded to three significant figures.

<sup>&</sup>lt;sup>b</sup> Data quality grades for Airborne, Dermal Uncovered, Dermal Covered and Hand are all Grade A or B, with the exception of one dermal replicate that has Dermal Uncovered Grade C (Dermal Covered for that replicate is Grade B). Data quality grades are defined in the text and in Versar (1992).

<sup>&</sup>lt;sup>b</sup> Median number of replicates was used for Dermal (non-hand).

<sup>&</sup>lt;sup>c</sup> Multipliers are explained in the Exposure Assessment section and in Powell (2002).

<sup>&</sup>lt;sup>d</sup> Dermal total includes addition of default feet value of 0.52 x (value for lower legs); ratio of feet/lower leg surface area (U.S. EPA, 1997).

<sup>&</sup>lt;sup>b</sup> Hand data multiplied by 0.1 for gloves (Aprea *et al.*, 1994). Inhalation data multiplied by 0.1 for use of respirator (NIOSH, 1987).

# Appendix 7: Backpack M/L/A, liquid (open pour)

Table 7-1. Description of PHED subsets <sup>a</sup>

Parameter	Specifications used to generate subsets	Actual characteristics of resulting subsets
Data Quality Grades <sup>b</sup>	A,B,C	A,B,C
Liquid Type	Not specified	Solution, Microencapsulated
Application Method	Backpack	Backpack
Mixing Procedure	Open	Open

<sup>&</sup>lt;sup>a</sup> Subsets of Mixer/Loader/Applicator data in the Pesticide Handlers Exposure Database (PHED). Parameter descriptions are from screens displayed in the PHED program.

Figure 7-1. Summary of results from the Pesticide Handlers Exposure Database (PHED) subset <sup>a</sup> SUMMARY STATISTICS FOR CALCULATED DERMAL EXPOSURES

SCENARIO: Long pants, long sleeves, gloves

PATCH	MICROGRAMS	PER AVERAGE	LB AI		
LOCATION	Mean	Coef of Var	Geo. Mean	Obs.	
HEAD (ALL)	345.2564	194.899	91.4483	11	Subset Name:
NECK.FRONT	178.6391	155.1078	38.2719	11	
NECK.BACK	1163.209	108.1731	611.9794	11	S20DERMAL.MLAP
UPPER ARMS	10116.4827	239.4633	257.2654	11	0.00.00.00.00.00.00.00.00.00.00.00.00.0
CHEST	275.4477	170.903	65.7564	11	
BACK	8918.1809	167.9854	1044.0635	11	
FOREARMS	153.593	184.2219	30.0425	11	
THIGHS	597.2782	282.8189	49.147	9	
LOWER LEGS	425.8878	230.6324	64.6874	9	

<sup>&</sup>lt;sup>a</sup> Subset criteria included actual and estimated head patches. Of the 11 head observations, all were actual.

Table 7-2. PHED data from dermal, hand, and inhalation subsets <sup>a</sup>

<b>Exposure Category</b>	Exposure (µg/lb AI handled) <sup>a</sup>	Replicates in subset <sup>b</sup>	Short-Term Multiplier <sup>c</sup>	Long-Term Multiplier <sup>c</sup>
Dermal (non-hand) <sup>d</sup>	22,300	11	6	2
Hand	9.68	11	6	2
Inhalation	17.5	11	6	2

<sup>&</sup>lt;sup>a</sup> Results from subsets of Mixer/Loader data in the Pesticide Handlers Exposure Database (PHED).

Table 7-3. Values Used in Short-Term and Long-Term Exposure Calculations <sup>a</sup>

	Short-Term	Long-Term
Total Dermal	$6(22,300 + 9.68) = 134,000 \mu\text{g/lb}$ AI handled	$2(22,300 + 9.68) = 44,600 \mu\text{g/lb AI handled}$
Inhalation <sup>b</sup>	$6(1.75) = 10.5 \mu g/lb AI handled$	$2(1.75) = 3.51 \mu g/lb AI handled$

<sup>&</sup>lt;sup>a</sup> Values from Table 7-2. Results rounded to three significant figures.

<sup>&</sup>lt;sup>b</sup> Data quality for Airborne, Dermal Uncovered, Dermal Covered are all Grade A or B; Hand data are all Grade C. Data quality grades are defined in the text and in Versar (1992).

<sup>&</sup>lt;sup>b</sup> Median number of replicates was used for Dermal (non-hand).

<sup>&</sup>lt;sup>c</sup> Multipliers are explained in the Exposure Assessment section and in Powell (2002).

<sup>&</sup>lt;sup>d</sup> Dermal total includes addition of default feet value of 0.52 x (value for lower legs); ratio of feet/lower leg surface area (U.S. EPA, 1997).

<sup>&</sup>lt;sup>b</sup> Inhalation data multiplied by 0.1 for use of respirator (NIOSH, 1987).

MLAP

# Appendix 8: Low Pressure Handwand M/L/A, Liquid Formulations

Table 8-1. Description of PHED subsets <sup>a</sup>

	Specifications used to generate	Actual characteristics of resulting
Parameter	subsets	subsets
Data Quality Grades b	A,B,C	A,B,C
Liquid Type	Emulsifiable concentrate, aqueous suspension, microencapsulated, solution, or undiluted liquid	Solution; Microencapsulated
Application Method	Low Pressure Handwand	Low Pressure Handwand.
Mixing Procedure	Not specified	All open

<sup>&</sup>lt;sup>a</sup> Subsets of Mixer/Loader/Applicator data in the Pesticide Handlers Exposure Database (PHED). Parameter descriptions are from screens displayed in the PHED program.

Figure 8-1. Summary of results from the Pesticide Handlers Exposure Database (PHED) subset <sup>a</sup> SUMMARY STATISTICS FOR CALCULATED DERMAL EXPOSURES

SCENARIO: Long pants, long sleeves, gloves

DATOH	MIADAADAMO	DED AUTRACE	ID AI		
PATCH	mickogkhms_	_PER AVERAGE			
LOCATION	Mean	Coef of Var	Geo. Mean	Obs.	
HEAD (ALL)	658.5361	136.7049	290.5017	80	Subset Name:
NECK.FRONT	137.9226	369.6483	18.9272	80	oasse name.
NECK.BACK	86.3274	429.9868	14.8349	79	S22DERMAL.MLA
UPPER ARMS	111.8313	232.934	32.6211	10	
CHEST	235.1875	185.929	48.9756	10	
BACK	163.797	202.4421	41.5723	10	
FOREARMS	40.9585	267.6492	9.412	10	
THIGHS	37.9878	115.1859	27.6737	- 9	
LOWER LEGS	66.9309	164.3135	30.0241	9	

<sup>&</sup>lt;sup>a</sup> Subset criteria included actual and estimated head patches. Of the 80 head observations, 10 were actual and 70 were estimated from nearby patches (Versar, 1992).

Table 8-2. PHED data from dermal, hand, and inhalation subsets <sup>a</sup>

<b>Exposure Category</b>	Exposure (µg/lb AI	Replicates in	Short-Term	Long-Term
	handled) <sup>a</sup>	subset b	Multiplier <sup>c</sup>	Multiplier <sup>c</sup>
Dermal (non-hand) <sup>d</sup>	1,570	10	6	2
Hand	10.4	10	6	2
Inhalation	22.8	10	6	2

<sup>&</sup>lt;sup>a</sup> Results from subsets of Mixer/Loader data in the Pesticide Handlers Exposure Database (PHED).

Table 8-3. Values Used in Short-Term and Long-Term Exposure Calculations <sup>a</sup>

	Short-Term	Long-Term	
Total Dermal	$6(1570 + 10.4) = 9,480 \mu\text{g/lb}$ AI handled	$2(1570 + 10.4) = 3{,}160 \mu\text{g/lb}$ AI handled	
Inhalation <sup>b</sup>	$6(2.28) = 13.7 \mu g/lb AI handled$	$2(2.28) = 4.56 \mu \text{g/lb AI handled}$	

<sup>&</sup>lt;sup>a</sup> Values from Table 8-2. Results rounded to three significant figures.

<sup>&</sup>lt;sup>b</sup> Data quality grades are defined in the text and in Versar (1992).

<sup>&</sup>lt;sup>b</sup> Median number of replicates was used for Dermal (non-hand).

<sup>&</sup>lt;sup>c</sup> Multipliers are explained in the Exposure Assessment section and in Powell (2002).

<sup>&</sup>lt;sup>d</sup> Dermal total includes addition of default feet value of 0.52 x (value for lower legs); ratio of feet/lower leg surface area (U.S. EPA, 1997).

<sup>&</sup>lt;sup>b</sup> Inhalation data multiplied by 0.1 for use of respirator (NIOSH, 1987).

## Appendix 9. Mitigation Measures Proposed by U.S.EPA

Several measures were proposed by U.S. EPA (2002) to mitigate occupational and environmental risks of methidathion use. Table 9-1 lists the protective clothing and PPE required for handlers according to current labels, and the clothing and PPE proposed in the mitigation measures.

Table 9-1. Handler Clothing and Personal Protective Equipment Listed on Existing Methidathion Labels and in Mitigation Measures Proposed in the Interim Reregistration Eligibility Decision <sup>a</sup>

	Existing Labels	Proposed in IRED	
Supracide 25WP <sup>b</sup>	Long-sleeved shirt and long pants	Airblast Applicator	
	Waterproof gloves	Coveralls over long-sleeved shirt and pants	
	Shoes and socks	Chemical-resistant gloves	
	Respirator	Chemical-resistant footwear and socks	
		Chemical-resistant headgear	
		Respirator	
		M/L and All Other Applicators <sup>c</sup>	
		Long-sleeved shirt and long pants	
		Chemical-resistant gloves	
		Shoes and socks	
		Protective eyewear	
		Respirator	
		Chemical-resistant apron for M/L	
Supracide 2E	Long-sleeved shirt and long pants	Airblast Applicator	
	Chemical-resistant gloves	Coveralls over long-sleeved shirt and pants	
	Shoes and socks	Chemical-resistant gloves	
	Protective eyewear	Chemical-resistant footwear and socks	
	Respirator	Chemical-resistant headgear	
		Respirator	
		M/L and All Other Applicators <sup>d</sup>	
		Long-sleeved shirt and long pants	
		Chemical-resistant gloves	
		Shoes and socks	
		Protective eyewear	
		Respirator	
		Chemical-resistant apron for M/L	

<sup>&</sup>lt;sup>a</sup> From Table 16, pp. 41-42 in IRED. No changes were proposed for M/L/A using backpack or handwand.

<sup>&</sup>lt;sup>b</sup> All WP products must be in WSP packaging (considered closed system for M/L).

<sup>&</sup>lt;sup>c</sup> Aerial applications of wettable powder products would be prohibited.

<sup>&</sup>lt;sup>d</sup> M/L in support of aerial applications are required to wear PPE and use a closed system. Closed cockpit is required for pilots. Use of human flaggers is prohibited.

# Appendix 9, Continued...

U.S. EPA (2002) proposed to mitigate handler exposures mainly by increasing PPE requirements and engineering controls, and to mitigate reentry exposure by increasing the REI to 3 days for all uses (note that California's REI regulation (3 CCR 6772) requires an extended REI of 30 days in citrus treated with methidathion). Table 9-2 shows the exposure estimates, including current estimates, from Table 9 for handlers and Tables 10 and 11 reentry workers, and the estimates for these scenarios if the proposed mitigation measures were finalized.

Table 9-2. Estimates of Pesticide Handler and Reentry Exposure to Methidathion Based on Mitigation Measures Proposed in the Interim Reregistration Eligibility Decision <sup>a</sup>

	Acute ADD	SADD	AADD	LADD	
Work Task	(mg/kg/day)	(mg/kg/day)	(mg/kg/day)	(mg/kg/day)	
<u>Aerial</u>					
$M/L^{b}$	1.15/ <b>0.960</b>	0.460/ <b>0.373</b>	0.038/ <b>0.031</b>	0.020/ <b>0.017</b>	
Applicator <sup>c</sup>	4.65/ <b>0.208</b>	1.55/ <b>0.044</b>	0.129/ <b>0.004</b>	0.069/ <b>0.002</b>	
Flagger <sup>d</sup>	1.90/ <b>NA</b>	0.475/ <b>NA</b>	0.040/ <b>NA</b>	0.021/ <b>NA</b>	
Airblast					
$M/L^{b}$	0.131/ <b>0.110</b>	0.053/ <b>0.043</b>	0.004/ <b>0.004</b>	0.002/ <b>0.002</b>	
Applicator <sup>e</sup>	5.86/ <b>5.03</b>	1.46/ <b>1.25</b>	0.122/ <b>0.104</b>	0.065/ <b>0.056</b>	
<u>Groundboom</u>					
$M/L^b$	0.158/ <b>0.132</b>	0.063/ <b>0.051</b>	0.011/ <b>0.009</b>	0.006/ <b>0.005</b>	
Applicator f	0.177	0.044	0.007	0.004	
Backpack sprayer					
$M/L/A^f$	0.191	NA	NA	NA	
Low-pressure handwand					
$M/L/A^f$	0.0034	NA	NA	NA	
Reentry					
Cotton Scout g	0.093/ <b>0.061</b>	0.0045/ <b>0.0030</b>	0.0011/ <b>0.0007</b>	0.0006/ <b>0.0004</b>	
Citrus Harvest/Thin <sup>f</sup>	0.007	0.0024	0.0008	0.0004	
Artichoke Thinning g	0.014/ <b>0.009</b>	0.0007/ <b>0.0004</b>	0.0001/ <b>0.00007</b>	0.00006/ <b>0.00004</b>	

<sup>&</sup>lt;sup>a</sup> New estimates in bold: old/new. "Old" estimates from Table 9 (handlers) and Tables 10 and 11 (for reentry). Not all scenarios were affected by proposed mitigation measures.

<sup>&</sup>lt;sup>b</sup> Mixer/Loader (M/L): Chemical apron would be required.

<sup>&</sup>lt;sup>c</sup> Closed cockpit and gloves would be required. CA regulation allows pilots in closed cockpit to omit gloves; new label assumed to supercede this and gloves factored into exposure estimate (otherwise, no change to estimate).

<sup>&</sup>lt;sup>d</sup> The use of human flaggers would be prohibited. NA: not applicable.

<sup>&</sup>lt;sup>e</sup> Coveralls and chemical apron would be required (major exposure is to head, however).

<sup>&</sup>lt;sup>f</sup> No change based on proposed mitigation measures.

g REI changed from 2 days to 3 days.